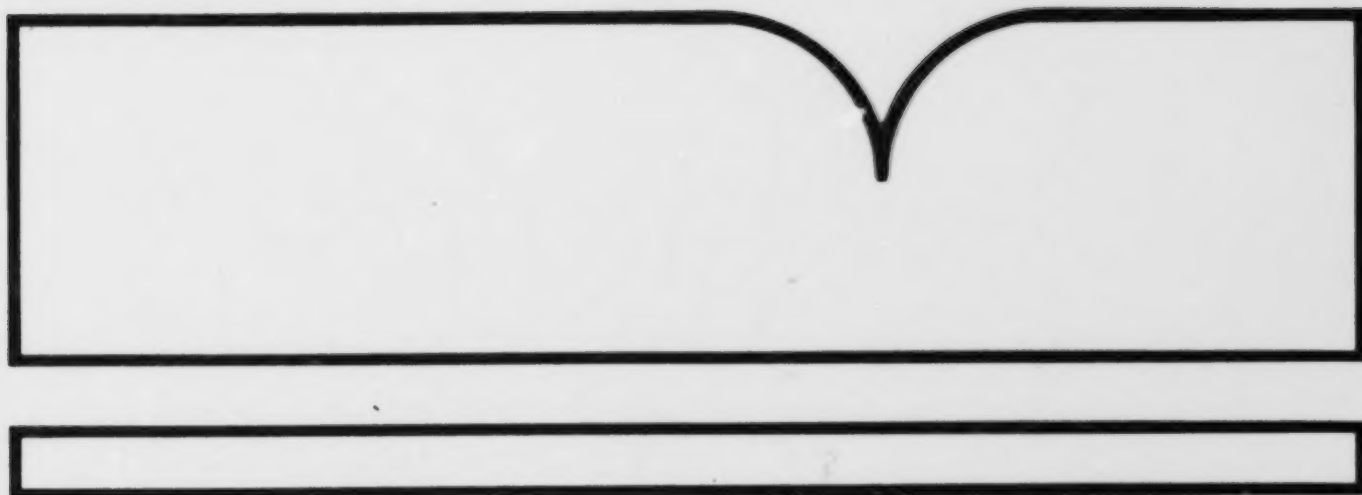


Receptor Model Technical Series
Volume 2. Chemical Mass Balance

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VOLUME II CHEMICAL MASS BALANCE

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RECEPTOR MODEL TECHNICAL SERIES

VOLUME II

CHEMICAL MASS BALANCE

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise and Radiation
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
Research Triangle Park, North Carolina 27711

July 1981

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ABSTRACT

Receptor Model Technical Series Volume II Chemical Mass Balance

Recent improvements in air sampling and analytical techniques have stimulated rapid growth in new techniques of source impact analysis using receptor models. These models "decode" the chemical fingerprints and variability of the ambient aerosol to back-calculate source impacts. Unlike source (dispersion) models that estimate source strengths from emission rate, meteorology and stack parameters, receptor techniques separate source contribution to the total, fine, coarse, or inhalable particulate mass using data from ambient aerosol measurements.

This document is the second of a series describing how receptor models can be used by State and local regulatory agencies to identify particulate source impacts. Volume I (EPA 450/4-81-016a) provides an overview of Receptor Model Applications, while Volume II focuses on the Chemical Mass Balance technique, model theory and input requirements. Case studies of applications in control strategies development are presented. Program design, ambient and source testing considerations, the use of receptor models in validating dispersion models and other potential application are discussed.

This document is intended to provide those responsible for the development of particulate control strategies, airshed management and source impact assessment with new information on the Chemical Mass Balance method.

EXECUTIVE SUMMARY

The purpose of this document is to provide those responsible for particulate control strategy development with a better understanding of the Chemical Mass Balance (CMB) Model. The CMB model is a receptor-oriented technique which may be used to apportion contributions to observed ambient levels of particulates among various sources (i.e., source apportionment). The report addresses (a) the technical basis of the model, (b) input requirements, (c) limitations, and (d) advantages/disadvantages. Case studies of how the CMB method has been applied by regulatory agencies in strategy development and dispersion model validation are also presented.

The Chemical Mass Balance Model allows the analyst to use ambient aerosol composition data, in association with composition data for airshed emission sources, to back-calculate the impact of specific sources, or source classes, at the receptor. This approach differs from dispersion modeling in that the latter attempts to determine source impacts at a receptor given data on source emission rates, stack parameters, source activity, and meteorology.

CMB methods can be applied in particulate source apportionment scenarios in which dispersion models cannot be used, such as the analysis of source impacts during actual 24-hour air pollution episodes, and the identification of sources which heretofore had not been adequately considered in emission inventories. CMB is limited in that it cannot be applied to problems in which the source does not yet exist (e.g., evaluation of proposed new stationary sources) or in analysis of impacts associated with changes in stack dispersion parameters (plume temperature, volume or height). Chemical mass balance can, however, be used to estimate future source strengths or to analyze the effect of alternative control strategies

if no changes in existing plume buoyancy, spatial or temporal characteristics of the emissions are assumed. Dispersion models have been used in concert with the CMB technique to detect errors in dispersion model emission inventories and modeling assumptions.

The CMB model's ability to separate source impacts depends on the particle size and chemistry of source emissions and the ambient aerosol. For example, lead is known to be a nearly unique tracer for leaded auto exhaust in many airsheds. Recent source emission composition studies have found that other chemical species also serve as useful tracers for other sources. Residual fuel oil combustion, for example, is often a unique source of fine particle (i.e., $<2.5\text{ }\mu\text{m}$ diameter) nickel and vanadium found in the fine particles, while fine particle manganese is a useful tracer for ferromanganese alloy production emissions. On a slightly more complex level, the ratios among chemical species emitted by a source (or the source "fingerprints") and those measured at an ambient air sampling site can be mathematically "matched" to identify the contributing sources. A simple, yet highly effective means of separating source impacts is through the use of fine ($<2.5\text{ }\mu\text{m}$) and coarse ($2.5\text{--}10\text{ }\mu\text{m}$) mode source and ambient particle measurement methods.

The ability of the CMB model to "match" the source emission and ambient aerosol "fingerprint" assumes, as do all receptor and source models, that (a) the mass of material deposited on the filter at the receptor is a linear combination of mass from each contributing source, and (b) the mass and chemical composition of the source emissions do not change from the time of emission to the time the particle is captured in sampling. Given these assumptions, a set of equations relating each chemical species measured in the ambient air to its potential

contributors are developed and solved to determine the likely source strength mix. The model uses an effective variance, least squares calculation routine to solve the set of equations and calculate the uncertainty in the source impact estimate.

CMB software is very inexpensive to run on commonly available computers. Model input requirements consist of fine and coarse mode measurements of source emissions and ambient aerosol chemistry. Measurements within each size fraction ideally include mass, about 25 elements, major ions, and organic and elemental carbon. Successful programs have, however, been conducted using only elemental data. The availability of size-resolved aerosol chemical composition data, either through EPA's inhalable particulate monitoring network or State/local agency programs, will likely increase dramatically in the near future as new, rapid analytical techniques become more widely used.

The source characterization data required by the model should, whenever possible, be obtained through a testing program of local sources. Literature values have, however, been widely used largely because good information on source emissions is either difficult to obtain or because some sources (e.g., motor vehicle exhaust) are difficult to test. If values from the literature are used, care must be taken to ensure that they are applicable to the area under study. New EPA programs designed to provide source composition data are expanding the base of source characterization data already available.

Although the focus of this volume is on the chemical mass balance model, the quality of the overall project design is undoubtedly the single most important factor in assuring that the strongest possible set of source impact evidence has

been gathered to support subsequent regulatory action. If, for example, the sampling sites used in the study are improperly located or if laboratory analytical data are of poor quality, the CMB results cannot be expected to provide a strong basis for agency policy. A sound program design, utilizing proven sampling instrumentation on an appropriate sampling schedule, competent lab analysis and data interpretation is of basic importance. Experience has shown that, whenever possible, several independent approaches to the source apportionment problem should be used to ensure that the strongest possible evidence is developed.

The accuracy of the CMB analysis can be evaluated through a number of independent approaches, some of which are based on the self consistency of the model results. Other means by which the results can be verified rely on agreement between CMB estimates and source activity, the transport of emissions and consistency with other impact estimates obtained through dispersion modeling, microscopy and other receptor method techniques. Results of CMB evaluations conducted on the Portland Aerosol Characterization Study suggest that source impacts can be estimated with relative uncertainties ranging from $\pm 5\%$ to $\pm 30\%$. Since uninventoried sources can be identified by the CMB analysis, it is important that inconsistencies between CMB results and other evidence be investigated and resolved.

The CMB technique has been applied in source apportionment studies of TSP, inhalable, fine and coarse mode particle fractions in at least 37 cities, 19 of which were specifically conducted to provide a basis for control strategy development programs. Source impacts resolved during these studies include:

Crustal sources	- soil and road dust, rock crushing, coal flyash
Transportation	- leaded, unleaded auto exhaust, diesel exhaust
Vegetative burning	- residential wood combustion, land clearing, slash burning, etc. (estimates have high uncertainties)
Calcium sources	- cement dust, limestone, slag dust
Marine aerosol	
Residual oil combustion	
Iron and steel production	
Ferromanganese production	
Hog fuel boilers	
Kraft and sulfite recover boilers	
Aluminum production	
Paint pigments	
Smelters (lead, copper and zinc)	
Municipal refuse incineration	
Secondary sulfate, nitrate and carbon	

Although coal flyash can be resolved from crustal sources in some airsheds, the ability of CMB methods to distinguish these two sources is highly dependent upon the chemical similarity of the emissions and the species included in the analysis protocol. Chemically similar sources, such as those included within the crustal, transportation, vegetative burning or calcium source groups, cannot be distinguished from one another by CMB methods alone. Further apportionment of the specific sources must be accomplished by other receptor-oriented techniques, source activity/transport analysis or microinventory methods. Although the

specific sources contributing to secondary aerosols also cannot be directly identified by CMB methods, that portion of the sulfate associated with primary emissions can be quantified, providing an upper limit estimate of the secondary sulfate concentration. The minimum costs associated with a source apportionment study using CMB is about \$5,000 for a single site, one year program (see Volume I, Chapter 3).

Chemical Mass Balance analysis has a wide range of potential applications. Uses to date have been limited to particulate source apportionment in support of control strategy programs, dispersion model validation, air resource management and apportionment of light extinction. Other potential uses include stationary source enforcement, control strategy tracking, policy development, PSD increment analysis, and identification of sources of toxic pollutants.

The use of CMB-derived source impact estimates, in concert with dispersion models, provides an extremely useful approach to dispersion model validation. By comparing selected source strengths estimated by each method, the analyst can easily identify which sources are being accurately estimated by the dispersion model and those source groups with impacts that are systematically over (or under) estimated. Sources included in the crustal (fugitive) dust group, often poorly simulated by dispersion models, lend themselves to CMB analysis by virtue of the group's unique coarse mode elemental "fingerprint." Given the importance of fugitive dust sources to particulate mass concentrations (and model performance), CMB-dispersion model analysis is especially helpful.

Properly applied, and with sufficient supportive evidence developed through independent approaches, chemical mass balance methods can provide important new

insights into the nature of a community's aerosol problem. As the technology expands, the cost associated with this method will come within the reach of more users, providing an important new tool to regulatory agencies.

ACKNOWLEDGEMENTS

The rapid growth in receptor model technology has been accomplished through the efforts of many researchers and regulatory professionals. While the current technology of receptor modeling is still in an early stage of development, those associated with its development see these methods as a tool of growing importance and potential to regulatory agencies.

Many of the concepts, research results and applications of the chemical mass balance technique discussed in this guideline are referenced to work by S. K. Freidlander, G. E. Gordon, J. G. Watson, J. A. Cooper, T. G. Dzubay, R. K. Stevens, the Air Quality Division staff of the Oregon Department of Environmental Quality and many others. Their work has advanced Dr. Freidlander's initial concepts to the technology's current state.

The principal author of this document is John E. Core of the Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. The comments and assistance of those individuals and organizations listed above as well as the Control Programs Planning & Development staff of OAQPS were important to the preparation of this document.

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Summary of Abbreviations

AAS	Atomic Absorption Spectroscopy
CMB	Chemical Mass Balance
Coarse Particles	Particles 2.5 - 10 μm mass median aerodynamic diameter
Fine Particles	Particle sizes ≤ 2.5 μm mass-median aerodynamic diameter
INAA	Instrumental Neutron Activation Analysis
PIXE	Particle Induced X-ray Emission
SEM-XRF	Scanning Electron Microscopy X-ray Fluorescence (computer automated)
TTFA	Target Transformation Factor Analysis
XRF	X-ray Fluorescence (either energy or wavelength dispersive)
XRD	X-ray Diffraction
μm	Mass median aerodynamic diameter, micrometers
Chemical Elements and Species	See Appendix I

1.0 INTRODUCTION

As demands to develop increasingly effective control strategy programs are brought to bear on State and local air pollution agencies, the need to more accurately identify sources contributing to poor ambient air quality become more apparent. Faced with pressure from many interested groups, the control officer responsible for development of particulate attainment strategies must provide convincing evidence that he understands the relative importance of different emission sources to the problem. He must also propose cost effective control programs that he, and the community, can adopt with confidence. Unless an effective case can be made to demonstrate the magnitude and identity of particulate sources causing the nonattainment problem, considerable doubt as to the effectiveness of new control programs can exist.

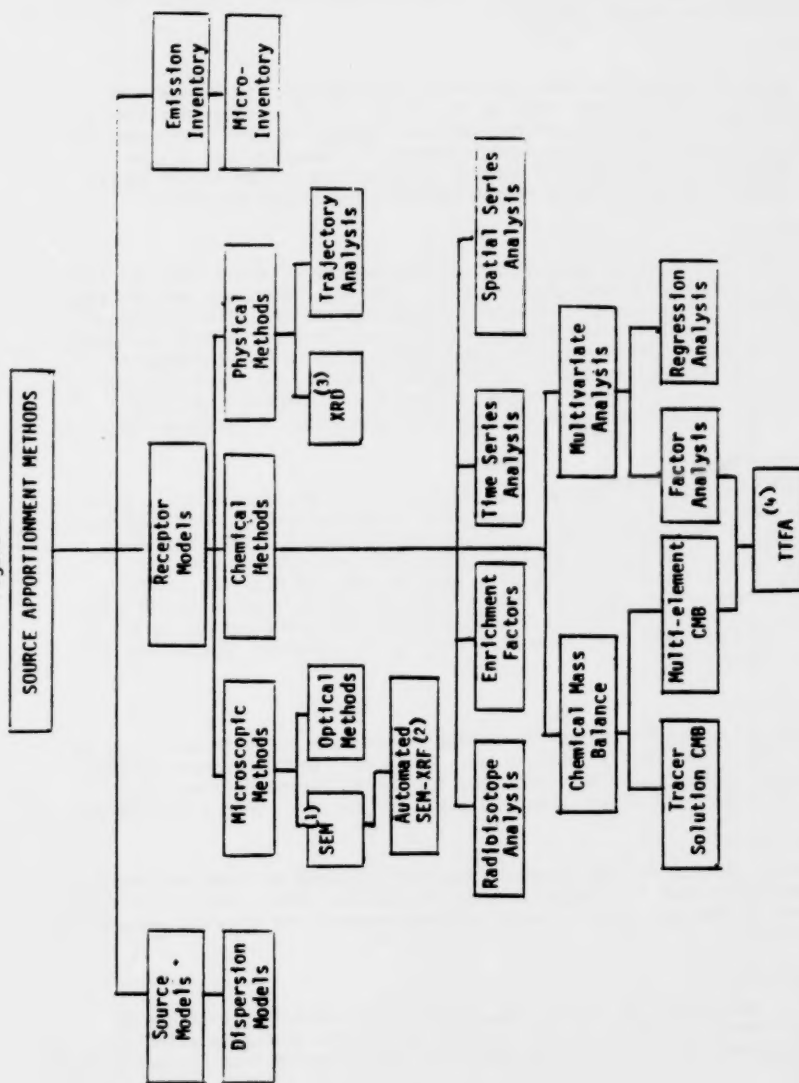
Until quite recently, traditional approaches have dictated that source impacts be identified by dispersion (source) modeling based on emission inventory and meteorological data. While these techniques will remain as an important tool in the regulatory effort, dispersion models have not met several critical program requirements. For example, their ability to apportion source impacts during actual, 24-hour worst case episodes or to assess impact from sources in complex terrain, are limited by difficulties in developing accurate particulate matter emission inventories and meteorological data bases. Further limitations in the ability of source-oriented models to estimate source contributions to the "background" aerosol typically limit the dispersion model's ability to apportion source impacts to about one-half of the measured aerosol mass. These constraints severely limit the analyst's ability to understand the true mixture of source strengths and the nature of the incoming air.

Recent advances in receptor oriented techniques (receptor models) are now beginning to supplement dispersion models as a major source apportionment tool.^{1,2} Receptor models are techniques that estimate the contributions of emission sources based on data obtained at the receptor. Figure 1 summarizes a number of source and receptor-oriented techniques which may be useful in devising effective strategies to reduce ambient levels of particulate matter. An overview of each of these techniques is provided in Volume I of this series (EPA-450/4-81-016a). Table 1 provides a glossary of receptor models. Chemical Mass Balance is one of a number of chemical receptor models. CMB can be applied using simple "tracer" methods (Section 3.1.1) or, in more typical applications, using multi-element solutions.

The CMB model has been applied in numerous source apportionment studies of total, coarse, fine and inhalable particulate mass. Recent applications have (a) successfully identified source classifications and chemical constituents that account for most of the measured aerosol mass, (b) been used by regulatory agencies in control strategy development programs, and (c) proven useful in dispersion model validation efforts.

Since the analyst's success in applying chemical mass balance methods is dependent upon the overall design of the source apportionment program, this document discusses topics ranging from analytical methods to emission inventory techniques. Other topics of importance to chemical mass balance programs presented in Volume I of this series include other receptor models, program design and management, typical program costs, and the application of receptor models to dispersion model validation.⁸ Those interested in applying CMB techniques should consult Volume I, as well as this document.

Figure 1



- (1) Scanning Electron Microscopy
- (2) X-Ray Fluorescence
- (3) X-Ray Diffraction
- (4) Target Transformation Factor Analysis

Table 1. Receptor Model Glossary

Chemical Mass Balance

This method matches source particle size and chemical "fingerprints" to those measured at the receptor to back-calculate the impact of specific sources or source classes of similar chemical composition. Given data on the ambient concentrations of several chemical species and the percent by weight of these species in the emissions from the sources, a set of equations is prepared and solved to determine the source impacts.

Enrichment Factors

Ambient aerosol composition data is used in association with a reference element (usually a crustal element such as Fe, Al or Si) to provide an estimate of the degree to which a specific ambient aerosol element has been "enriched" by an anthropogenic source. If the "enriched" element is known to be a unique tracer for a specific source, and the concentration of the tracer in the source emissions is known, a crude estimate of the source's impact can be made.³

Microscopic Methods

Particle identification by optical microscopy was one of the first, and the most widely used method of source apportionment. Current technology has expanded to include computer-driven scanning electron microscopy coupled with x-ray fluorescence analysis to provide a particle-by-particle analysis of ambient particulate filters. As a consequence, particle identification methods traditionally founded on particle size shape, color, birefringence, and surface properties has been expanded to include elemental composition and rapid, computer assisted analysis permitting large numbers of particles to be analyzed at minimum cost.

Multivariate Methods

Statistical methods that include factor analysis, regression methods, principle component and cluster analysis techniques. These methods extract information on source impacts on the basis of the variability of chemical species measured within a large set of particulate samples. Given the premise that chemical species emitted from a specific source will vary in time (as measured at the receptor) in the same manner, multivariate methods detect the common variability of the chemical species. The analyst then identifies the contributing source by comparing those species with similar variability to the chemical composition of sources within the airshed.

Radioisotope Analysis

Measurement of carbon-14/carbon-12 isotope ratios have recently been used to distinguish "modern" from fossil fuel carbon. Using this method, carbon emitted from contemporary sources (wood burning, leaf fragments, fireplaces) has been distinguished from auto and diesel exhaust, coal and fuel oil carbonaceous aerosols.⁴

Spatial Series Analysis

Spatial relationships between aerosol chemistry measured at numerous receptors can provide important clues to likely contributing sources when viewed in relation to emission density maps and given a basic understanding of the chemical composition of source emissions.⁵

Time Series Analysis

Qualitative indications of source impacts based on temporal variations in aerosol mass and chemistry can be used, in association with source emission activity and transport data, to gain insight into likely source impacts over time.⁵

X-Ray Diffraction

Quantitative identification of crystalline substances in the coarse mode (>2.5 μ m) by XRD has enabled analysts to determine impacts from fugitive emission sources with reasonable accuracy ($\pm 25\%$) for moderate to heavily loaded filters.^{6,7}

2.0 CHARACTERISTICS OF AMBIENT AEROSOL AND SOURCE PARTICULATE EMISSIONS

Since our ability to "decode" ambient particulate chemical composition measurements is central to the success of the CMB model, a thorough understanding of the aerosol properties, emission composition, transport and source operating characteristics is highly important to the success of any source apportionment study. A brief review of the nature of ambient aerosol and source emission characteristics, as related to CMB applications, is therefore helpful in understanding and designing source apportionment studies.

2.1 Characteristics of Ambient Aerosols

The urban aerosol is a continuous varying mixture of solid and liquid particles that vary in size, shape, chemical composition and specie concentration because of (a) variations in the nature and strength of local sources, (b) differing chemical and physical processes of particle condensation, deposition, growth and decay, (c) variations in the mixing and dilution capacity of the air, (d) the previous history of an air mass and its burden of transported particles contributed by upwind sources, and (e) scavenging processes such as dry and wet deposition. Although aerosols typically range from about 0.002 μm to about 100 μm , regulatory authorities are usually most concerned with those particles within the size range captured by the hi-vol sampler (0.01 to about 30 μm) and, more recently, by the fine particle (0.01 to 2.5 μm) and coarse particle (2.5 to 10 μm) modes collectively referred to as inhalable particulate matter (0.01 - 10 μm).

The distribution of ambient aerosols measured in urban areas is typically bimodal in nature, with a fine particle mode peaking at about 0.3 μm and the coarse mode centered at about 5 to 10 μm . The minimum in the distribution

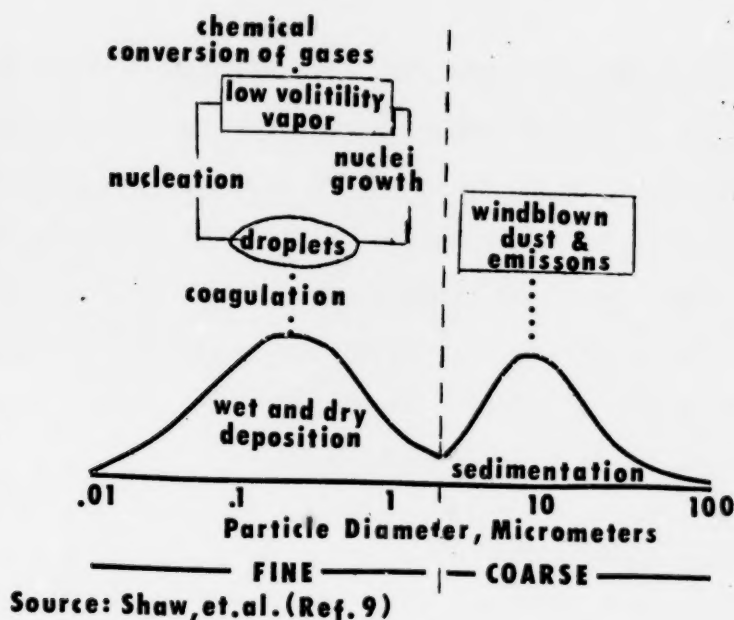


Figure 2. Typical Urban Particle Size Mass Distribution

usually occurs at about 2 μm . Figure 2⁹ is a typical particle size distribution. Properties of the aerosol are noted.

The relative abundance of the fine and coarse mode aerosol can change rapidly in terms of mass, chemical composition and physical properties depending on the nature of the contributing sources. Generally, the fine particle fraction is composed of anthropogenic source aerosols which are more hazardous to the public health, are more important in reducing visibility and which contain the majority of the secondary aerosols. Coarse particles tend to be quite different in source origin and chemical composition. Fugitive dust sources from natural wind entrainment of soils, dust entrained by vehicle movement and emissions from industrial material handling largely dominate, although emissions of incomplete combustion, plant tissues and grinding operations can also be important sources.

Although the chemical composition of urban aerosol varies greatly between communities and by size fraction, it is typically composed of about 35% carbon, 25% oxygen, 10% silicon, 5% hydrogen, sulfur, calcium and a host of other ions and trace elements.¹⁰ Figure 3 shows the average composition of urban particulate matter, while the concentration of trace elements in the fine and coarse mode are listed in Table 2.¹¹ Figure 3 also shows the elemental composition patterns of total and fine particle fractions in Portland, Oregon.

A closer examination of the data shows that the fine fraction is largely composed of sulfate, nitrate, lead, bromine and carbon components. The coarse mode is dominated by Al, Si, Ca, Fe, Ti and K, often associated with fugitive dust sources. The fact that most combustion, condensation, secondary aerosols and post-control industrial process emissions are found in the fine particle fraction provides a strong incentive to use size segregating dichotomous samplers to isolate these sources from the fugitive dust impacts associated with the coarse mode particulate.

2.2 Source Emission Characteristics

An accurate physical and chemical characterization of source emissions is probably the most important factor to the successful use of the CMB method. Proper application of the method is highly dependent upon a reasonably accurate knowledge of the chemical composition of the source emissions. It requires that all major sources of ambient aerosol mass be characterized, preferably through a testing program of local sources. As a less desirable alternative, literature values can be used if care is taken to ensure that the data are applicable to the sources in the study area. For example, the concentration of fine particle Ni and V in residual fuel oil fired boiler emissions is dependent upon the concentration

Figure 3
Ambient Aerosol Composition Patterns

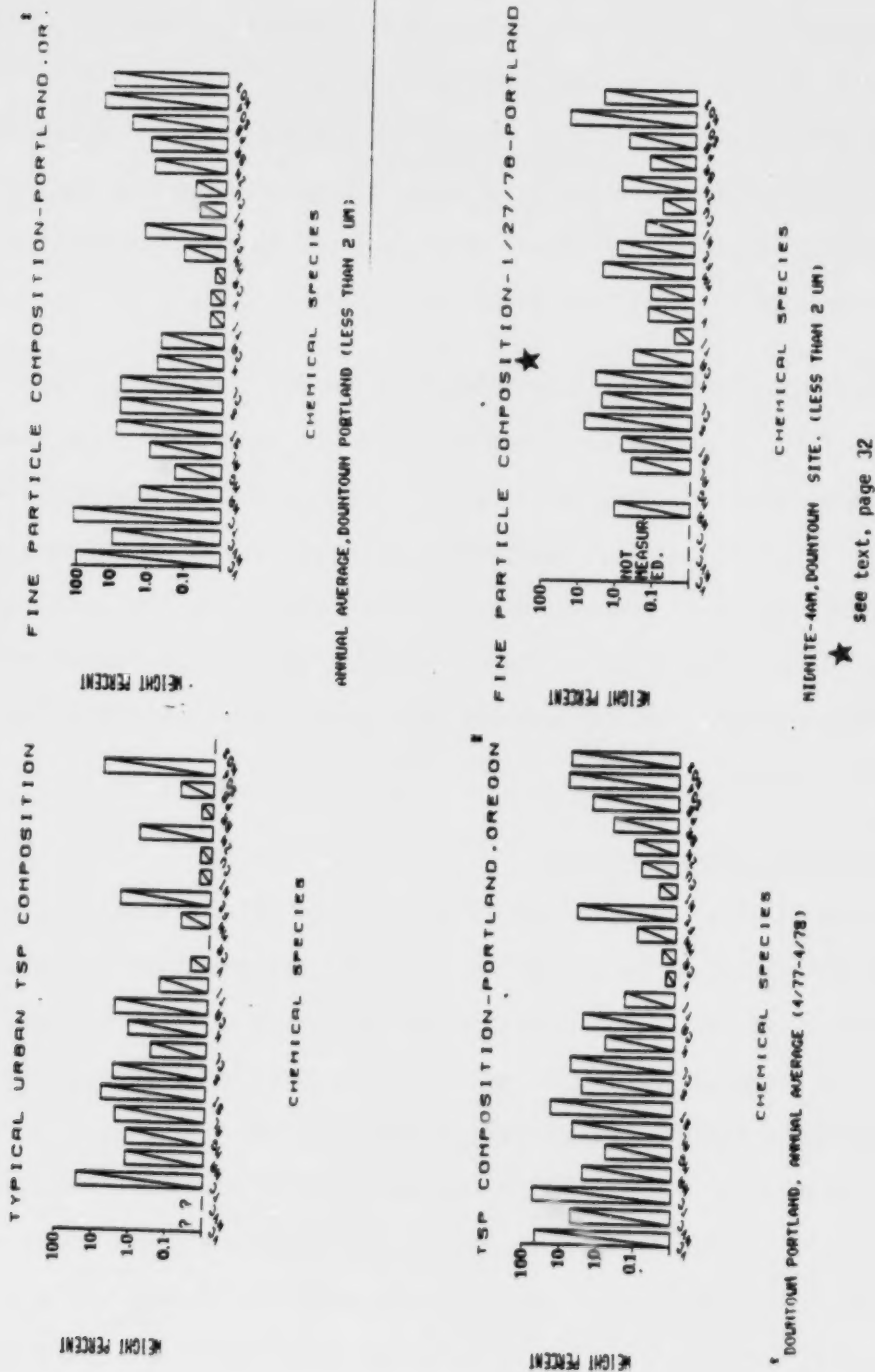


Table 2. Typical Chemical Composition of Fine and Coarse Mode Aerosols from Selected Urban Areas ($\mu\text{g}/\text{m}^3$).

Species	Charleston, WV (a)		St. Louis, MO (b)		St. Louis, MO (c)		Portland, OR (d)		Portland, OR (e)		Washington, DC (f)	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Mass	33.400	27.100	23.100	23.100	17.000	16.200	25.000	39.000	14.300	16.300	-	-
C	5.200	3.200	-	-	-	-	6.800	6.900	4.100	3.000	-	-
N	3.300	0.460	-	-	-	-	0.350	0.360	0.250	0.240	-	-
SO_4^{2-}	9.900	1.020	-	-	-	-	2.500	1.360	1.830	0.710	1.200 ^g	8.900
Na	0.190	0.034	-	-	-	-	0.280	0.750	0.250	0.400	0.120	0.290
Al	0.074	1.100	0.170	0.980	0.070	0.600	0.190	1.900	0.110	0.690	0.120	0.870
Si	0.410	2.800	0.250	3.400	0.170	2.400	0.200	6.000	0.180	2.200	-	-
Cl	0.040	0.080	0.165	0.320	0.020	0.100	0.840	0.810	0.390	0.320	0.190	0.340
K	0.100	0.290	0.180	0.300	0.110	0.240	0.150	0.320	0.120	0.155	0.090	0.220
Ca	0.100	0.960	0.130	2.600	0.100	1.800	0.120	1.270	0.065	0.410	0.060	0.580
Ti	0.011	0.077	-	0.190	-	0.055	0.009	0.160	0.004	0.048	0.011	0.075
V	<0.002	0.002	-	-	-	-	0.012	0.012	0.004	0.003	0.031	0.013
Mn	0.007	0.010	0.024	0.027	0.005	0.014	0.032	0.055	0.008	0.016	0.009	0.012
Fe	0.015	0.590	0.240	1.000	0.110	0.515	0.200	1.800	0.060	0.430	0.150	0.610
Cu	0.020	0.004	0.045	0.011	0.010	0.003	0.026	0.058	0.017	0.052	0.140	0.007
Zn	0.032	0.010	0.140	0.110	0.060	0.024	0.062	0.070	0.019	0.012	0.098	0.018
As	0.026	-	-	-	-	-	0.004	0.001	0.003	-	0.002	0.001
Se	0.007	-	0.003	-	0.002	-	0.002	0.001	0.001	-	0.002	0.001
Br	0.150	0.039	0.145	0.030	0.025	0.005	0.240	0.095	0.038	-	0.260	0.095
Pb	0.660	0.120	0.530	0.190	0.170	0.030	0.645	0.410	0.100	0.040	-	-
											0.440	

Source: Controlling Airborne Particles, Reference 11

- (a) Fine < 3.5 μm , coarse 3.5-20 μm
 (b) Fine < 2.4 μm , coarse 2.4-15 μm
 (c) Measured value was 5, assumed to be all SO_4^{2-}
 (d) Fine < 2 μm , coarse 2-30 μm
 (e) Measured as NO_3^- only
 (f) Fine < 2 μm , coarse > 2 μm . Values for SO_4^{2-} , NO_3^- , Pb not size-resolved
 (g) Sum of N as NH_4^+ and NO_3^-

of these elements in the crude oil from which the fuel is refined. If the actual concentration of Ni and V (or the Ni/V ratio) in local fuel oil is significantly different than that associated with the literature value, emissions data, the reported data may not be directly applied. In recognition of this potential source of error, Heisler¹² applied corrections to Ni and V literature values reported for Portland, Oregon, residual oil combustion sources during his studies of Denver aerosol. Corrections to the Portland source data were applied in accordance with the Ni and V concentrations in Portland and Denver fuel oils.

Successful application of the CMB method ideally requires that the source emissions within the airshed each emit unique chemical "fingerprints," each of which meet the following criteria:

- ° High concentrations of key chemical species which are stable over time and with atmospheric dilution.
- ° Concentration of key species should be low in other major sources and in the natural background.
- ° High analytical sensitivities at low cost using rapid laboratory techniques.
- ° Low analytical filter blanks for important chemical species.

Chemical species (elements, ions, carbon subclasses, organic compounds, etc.) that meet these criteria are referred to as "tracer" elements which, when included in the CMB model are referred to as "fitting" elements. It is those elements that are used in the model computations to estimate the source impacts

(see Section 3.1). Table 3 lists several chemical species that have served as tracer elements in past studies.

The chemical composition of source emissions is often variable in time and may be a function of the process cycle (industrial emissions), combustion efficiency, control system efficiency, variations in the chemical composition of input materials, residence time of the particles from initial generation to emission release, volatility of the species emitted, and many other factors. Although many studies of source emission chemical composition have been done, few source test programs have been targeted specially for use with CMB studies. Typical difficulties associated with the use of many "non-CMB" source composition studies in the literature include:

- ° Inadequate documentation of the source input materials, chemical composition, operating conditions or process cycle variations.
- ° Incomplete laboratory analysis of the particle mass. Typically omitted measurements include many trace elements, carbon (and carbonaceous aerosol subclasses) and major ionic species such that the sum of the species measured seldom approximate the measured mass.
- ° Lack of size segregated samples into size fractions consistent with those measured by typical ambient monitoring systems.
- ° Source composition data reported in units inconsistent with CMB requirements (data should be reported as mg/g, $\mu\text{g/g}$ or as a weight % of total mass).

Table 3. Qualitative Source Impact Indicators

Source	Indicator	Size Fraction	Analysis Method**	Sampling Method**
Motor vehicles	Pb, Br	Fine, coarse or total	1	Dichotomous
Soil and road dust	Sf, Al	Coarse	1,2,3,5	Dichotomous
Residual oil comb.	Ni, V	Fine	1	Dichotomous
Tire rubber	Styrene butadiene rubber (SBR)	Coarse	3,4	Dichotomous or hi-vol
Vegetative burning and fossil fuel comb.	$^{12}C^{14}C$ analysis	Fine	5	Hi-volume impactor
Aluminum production	F or F ⁻	Fine, coarse or total	1,6	Dichotomous or hi-vol
Vegetative burning	$K_{Fe} > 10$	Fine	1	Dichotomous
Limestone, cement or lime	Ca	Coarse	1	Dichotomous
Paint pigments	Ti/Fe > 0.3	Coarse	1	Dichotomous
Galvanizing and refuse incineration	Zn	Fine	1	Dichotomous
Diesel emissions	Ba or Pb with diesel auto emissions	Fine	1	Dichotomous
Marine aerosol snow control	Na, Cl	Coarse	1,6	Dichotomous or hi-vol
Coal, flyash, nonferrous smelters	Se, As	Fine	1	Dichotomous
Fertilizer production	P	Coarse or total	1	Dichotomous or hi-vol
Lead smelter	High Pb, $\frac{Br}{Pb} > 0.1$	Fine	1	Dichotomous

*Analysis Method Key

1. Elemental analysis by XRF, INAA or AA
2. X-ray diffraction
3. Optical microscopy

4. Gas chromatography analysis
5. SEM-XRF
6. Ion chromatography or colorimetric methods

** Size segregating sampler with membrane filters unless otherwise stated

° Condensible hydrocarbon emissions which form a major portion of emissions from many low temperature combustion processes, are seldom measured.

° Quantitative estimates of the uncertainty of source composition data are typically not found.

In the case of high temperature stack emissions, volatile species (Hg, Ag, Se, halogens, Cd, Sb and organic hydrocarbons) are difficult to accurately characterize and are subject to considerable measurement error. Unless special care is given to volatile species during the testing program, many of these species will not be correctly estimated. In-plume sampling methods using aircraft and tethered balloon sampling platforms have been used to minimize volatile specie losses associated with in-stack testing.

Information on tracer elements and other source indicator components is extremely useful in designing CMB source apportionment studies. Table 3 lists several characteristic indicators of source emissions which may be useful in selecting those species to be measured in a program. Although CMB studies have been conducted by many investigators using only aerosol elemental data,¹³⁻¹⁸ recent studies conducted within the State of Oregon¹⁹⁻²³ have found inclusion of carbon subfractions within the source and ambient measurement programs, to be useful in apportioning impacts from vegetative burning and in accounting for all of the ambient aerosol mass.

Source composition data typically used in CMB studies are shown in Tables 4,²⁴ 5,²⁰ 6,¹⁷ and 7.²² Note that the species included in the source composition input data can be normalized to mass (Tables 4, 6, 7) or to a specific element (Table 5). Figure 4 compares the chemical composition "fingerprints" of several

Table 4. Source Composition Data** - St. Louis, Missouri
(weight percent of mass)

Element	Ammonium Sulfate	Motor Vehicles	Crustal Shale	Crustal Limestone	Paint Pigment	Steel Industry
C		56.3	1.5	11.4		
Na			0.96	0.04		
Mg		0.6	1.5	4.7		0.3
Al			8.0	0.42		1.1
Si			27.3	2.4		0.7
P		.009	0.07	0.04		0.1
S	24.2	.06	0.24	0.12		
Cl		1.9	0.018	0.015		
K			2.66	0.27		
Ca			2.21	30.2		1.2
Ti			0.46	0.04	42.2	
V			0.013	0.002		
Cr			0.009	0.001		
Mn		0.06	0.085	0.11	0.4	3.1
Fe		0.1	4.72	0.38	20.4	57.0
Ni			0.001	0.002		
Cu			0.005	-		
Zu		0.3	0.01	0.002		
Se						
Br		3.7		0.001		
Rb			0.014			
Sr			0.03	0.061		
Cd						
Sn			0.001			
Sb						
Ba		0.09	0.058	0.001		
Pb		14.8	0.002	0.001		
Other*	75.8	21.5	50.1	49.8	37.0	36.5
* Includes H, N, O						

Source: Dzubay (Ref: 24)

** Total Suspended Particulate

Table 5. Source Composition Data, Portland, Oregon (weight percent of mass)*

Fine Particulate Composition (<2.0 μ)												
Source	OC	EC	NO ₃	SO ₄	F	Na	Mg	Al	Si	S	Cl	K
1. Marine	0.0	0.0	0.0	10	0.0	40.0	4.8	0.0	0.0	3.3	40.0	1.0
2. Continental Dust	4.32	0.59	0.0	0.0	0.0	0.69	1.76	11.7	25.4	0.07	0.0	1.0
3. Urban Dust	11.8	1.85	0.0	0.42	0.0	1.25	1.30	8.84	22.3	0.37	0.0	1.0
4. Leaded Auto Exhaust	50.0	3.8	0.91	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.03
5. Residual Oil Comb.	7.0	3.1	0.65	48.1	0.05	3.5	0.0	1.1	0.82	0.4	3.0	0.072
6. Vegetative Burn 1	59.0	3.5	5.1	1.6	0.0	0.65	0.0	0.53	0.96	13.3	0.0	0.28
7. Vegetative Burn 2	47.0	4.4	2.0	5.0	0.32	0.33	0.0	1.44	0.89	0.48	5.55	0.60
8. Kraft Recovery Boiler	1.7	0.22	0.0	40	0.0	12.7	0.63	0.45	0.49	1.6	9.9	6.5
9. Sulfite Recovery Boiler	0.0	0.0	0.3	56	0.0	2.5	0.73	0.0	0.15	11.7	1.8	1.5
10. Hog Fuel Boiler	0.0	0.0	0.51	33.8	0.15	3.4	0.0	0.24	0.40	12	0.58	30.0
11. Aluminum Processing	3.9	2.3	0.41	4.4	6.0	4.1	2.8	27.0	0.76	8.8	9.5	22.4
12. Steel Electric Furnace	0.0	0.0	0.0	2.5	0.0	1.26	6.5	0.65	5.0	1.4	1.33	0.22
13. Ferromanganese	9.0	1.5	5.7	4.2	0.29	3.1	0.0	0.64	0.99	1.9	1.85	0.92
14. Carborundum	13.6	55.0	1.6	16.0	0.05	0.12	0.78	0.35	3.5	4.8	1.7	10.5
15. Glass Furnace	0.0	0.0	0.62	65.0	0.54	9.2	0.0	0.19	0.25	11.3	0.06	1.37
16. Carbide Furnace	7.3	1.2	0.57	3.2	0.0	0.92	2.4	0.58	2.5	1.6	1.05	1.25

Coarse Particulate Composition (2.0-20 μ m)												
Source	OC	EC	NO ₃	SO ₄	F	Na	Mg	Al	Si	S	Cl	K
1. Marine	0.0	0.0	0.0	10	0.0	40	4.8	0.0	0.0	3.3	40.0	1.4
2. Continental Dust	4.32	0.59	0.01	0.004	0.002	1.3	1.2	7.2	29.7	0.0	0.0	2.2
3. Urban Dust	3.34	1.55	0.02	0.074	0.008	1.75	1.54	6.6	28.0	0.0	0.0	1.03
4. Leaded Auto Exhaust	50.0	3.8	0.91	1.3	0.0	0.0	0.0	1.1	0.82	0.4	3.0	0.72
5. Residual Oil Comb.	7.0	3.1	0.65	48.1	0.052	3.5	0.0	0.53	0.96	13.3	0.0	0.28
6. Vegetative Burn 1	59.0	3.5	5.1	1.6	0.0	0.65	0.0	1.44	0.89	0.43	5.55	0.60
7. Vegetative Burn 2	47.0	4.4	2.0	5.0	0.32	0.33	0.0	0.45	0.49	1.6	9.9	6.5
8. Kraft Recovery Boiler	15.8	1.8	0.0	11.8	0.0	5.3	0.0	0.28	0.13	3.3	2.9	0.40
9. Sulfite Recovery Boiler	0.0	0.0	0.3	56.0	0.0	2.5	0.73	0.0	0.40	12.0	0.58	30.0
10. Hog Fuel Boiler	11.1	4.3	0.2	1.5	0.11	0.69	0.46	0.28	0.96	0.59	0.83	1.3
11. Aluminum Processing	0.0	1.6	0.0	1.7	4.2	2.4	2.7	31.3	0.097	0.0	1.2	0.0
12. Steel Electric Furnace	0.0	0.0	0.0	2.5	0.0	1.26	6.5	0.65	5.0	1.95	1.85	0.92
13. Ferromanganese	9.0	1.5	5.7	4.2	0.29	3.1	0.0	0.65	0.99	1.7	1.42	10.5
14. Carborundum	4.6	24.0	0.83	1.6	0.0	0.26	0.0	0.65	12.0	0.41	0.99	0.72
15. Glass Furnace	0.0	0.0	0.62	65.0	0.054	9.2	0.0	0.19	0.25	11.3	0.06	1.37
16. Carbide Furnace	4.5	3.6	0.0	0.93	0.0	0.43	1.25	0.86	2.9	0.54	0.96	0.48

SOURCE: Cooper (Reference 20)

SOURCE: Cooper (Reference 20)

* See Appendix I

Table 5. Source Composition Data, Portland, Oregon (weight percent of mass) (Continued)*

Source	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
1. Marine	1.04	---	---	---	---	---	---	---	---	.20	---	---
2. Continental Dust	.93	.76	.025	.03	.20	6.8	.0092	.02	.041	0.0	.006	---
3. Urban Dust	2.44	.64	.023	.045	.123	6.0	.0093	.030	.11	0.0	.37	---
4. Leaded Auto Exhaust	1.25	0.0	0.0	0.0	0.0	2.1	.018	.073	.35	.020	20.0	~10
5. Residual Oil Comb.	1.58	.11	3.44	.047	.046	2.97	5.36	.075	.40	0.13	.11	~80
6. Vegetative Burn 1	1.07	0.0	0.0	0.0	.12	.19	0.0	.09	0.0	.053	0.0	90
7. Vegetative Burn 2	.92	.07	0.0	.012	.047	.054	0.0	.054	0.0	.045	0.0	~99
8. Kraft Recovery Boiler	0.0	.006	.001	.28	.03	1.2	.13	.021	0.69	.13	.013	87
9. Sulfite Recovery Boiler	2.0	.01	0.0	0.0	.054	.066	0.0	.016	.017	0.0	0.0	~90
10. Hog Fuel Boiler	5.6	0.0	0.0	.015	.51	1.26	.0067	.12	.73	.055	.42	78
11. Aluminum Processing	.33	.04	.064	0.0	.011	.45	.19	.044	.015	.037	.012	56
12. Steel Electric Furnace	6.2	.20	.06	2.1	8.7	32.0	.07	.28	1.2	0.0	.76	92
13. Ferromanganese	1.3	.046	.024	.42	17.3	2.1	0.0	.036	.58	.16	.045	92
14. Carborundum	.14	.014	.007	.009	.035	.33	.004	.019	.004	.0063	.38	82
15. Glass Furnace	.30	0.0	.0047	.19	.0021	.02	0.0	.0047	.011	0.0	0.0	93
16. Carbide Furnace	30.0	0.0	.006	0.0	.042	.54	.022	.020	.015	0.0	.008	55

Source	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
1. Marine	1.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	.20	0.0	---
2. Continental Dust	1.4	0.82	.017	.01	.085	4.78	.009	.02	.031	0.0	.042	---
3. Urban Dust	3.0	1.01	.027	.045	.10	5.73	.004	.03	.11	0.0	.37	---
4. Leaded Auto Exhaust	1.25	0.0	0.0	0.0	0.0	2.1	.018	.073	.35	.008	.37	~90
5. Residual Oil Comb.	1.58	.11	3.44	.047	.046	2.97	5.36	.075	.40	5.0	20.0	~20
6. Vegetative Burn 1	1.07	0.0	0.0	0.0	.12	.19	0.0	.09	0.0	.013	.11	10
7. Vegetative Burn 2	.92	.07	0.0	.012	.047	.054	0.0	.054	0.0	.053	0.0	~1
8. Kraft Recovery Boiler	.36	0.0	0.0	.48	.52	1.84	.22	.06	0.0	.45	0.0	~1
9. Sulfite Recovery Boiler	2.0	.01	0.0	0.0	.054	.066	0.0	.016	0.0	.56	0.0	13
10. Hog Fuel Boiler	5.2	.097	.0055	.0073	.29	.92	0.0	.23	.017	0.0	0.0	~10
11. Aluminum Processing	.81	.076	.040	.016	0.0	.38	.21	.14	.039	.0013	.020	~20
12. Steel Electric Furnace	6.2	.20	.06	2.1	8.7	32.0	.7	.28	1.2	.12	0.0	42
13. Ferromanganese	1.3	.046	.024	.042	17.3	2.1	0.0	.036	.58	0.0	.76	8
14. Carborundum	.57	.033	.012	.004	.029	.27	.017	.055	0.0	.16	.045	8
15. Glass Furnace	.30	0.0	.0047	.19	.0031	.02	0.0	.0047	.011	0.11	0.0	19
16. Carbide Furnace	25.8	0.0	.009	0.0	.036	.33	.021	.004	0.0	.0063	.38	7
										0.0	0.0	45

* See Appendix I

Table 6. Source Composition Data* - Washington, DC
(Normalized to Reference Element)

Element	Soil	Marine	Coal Combustion	Oil Combustion	Refuse Combustion	Motor Vehicles
Na	5.3×10^{-2}	≈ 1.0	1.6×10^{-2}	5.3×10^{-1}	6.8×10^{-1}	--
K	1.9×10^{-1}	3.6×10^{-2}	1.3×10^{-1}	1.9×10^{-2}	--	--
Mg	9.3×10^{-2}	1.3×10^{-1}	5.2×10^{-2}	1.7×10^{-1}	1.1×10^{-1}	--
Ca	8.1×10^{-2}	3.8×10^{-2}	9.0×10^{-2}	3.5×10^{-1}	1.4×10^{-1}	5×10^{-2}
Ba	8.7×10^{-3}	2.8×10^{-6}	9.0×10^{-3}	8.3×10^{-2}	5.8×10^{-3}	1.3×10^{-2}
Cl	3.3×10^{-3}	1.81	2.0×10^{-3}	5.3×10^{-1}	1.67	1.0×10^{-1}
Br	1.2×10^{-4}	6.2×10^{-3}	4.0×10^{-3}	2.3×10^{-3}	1.3×10^{-2}	3.8×10^{-1}
I	7.0×10^{-5}	5.7×10^{-3}	4.0×10^{-3}	--	--	--
Al	≈ 1.0	9.5×10^{-7}	≈ 1.0	1.8×10^{-2}	1.2×10^{-1}	--
Sc	1.8×10^{-4}	3.8×10^{-9}	3.5×10^{-4}	8×10^{-6}	1.1×10^{-5}	--
Ti	6.4×10^{-3}	9.5×10^{-8}	6.0×10^{-2}	1.1×10^{-3}	2.0×10^{-2}	--
V	1.3×10^{-3}	1.9×10^{-7}	3.0×10^{-3}	≈ 1.0	2.6×10^{-4}	--
Cr	9.8×10^{-4}	4.7×10^{-9}	1.6×10^{-3}	2.6×10^{-3}	4.1×10^{-3}	--
Mn	1.6×10^{-2}	1.9×10^{-7}	3.0×10^{-3}	4.3×10^{-3}	6.1×10^{-3}	--
Fe	6.3×10^{-1}	9.5×10^{-7}	7.0×10^{-1}	1.2×10^{-1}	5.4×10^{-2}	5×10^{-2}
Co	2.7×10^{-4}	4.8×10^{-8}	4.8×10^{-4}	7.0×10^{-3}	5.5×10^{-5}	--
Ni	5.6×10^{-4}	1.9×10^{-7}	2.0×10^{-3}	1.7×10^{-1}	1.3×10^{-3}	--
Cu	2.8×10^{-4}	2.8×10^{-7}	4.0×10^{-3}	3.5×10^{-2}	1.3×10^{-2}	--
Zn	1.4×10^{-3}	9.5×10^{-8}	5.0×10^{-3}	7.0×10^{-1}	≈ 1.0	1.5×10^{-2}
As	7.5×10^{-5}	2.8×10^{-7}	6.0×10^{-3}	1.2×10^{-3}	2.0×10^{-3}	--
Se	1.1×10^{-6}	3.8×10^{-7}	1.5×10^{-3}	1.5×10^{-3}	3.1×10^{-4}	--
Cd	1.3×10^{-6}	1×10^{-8}	2.6×10^{-4}	1.2×10^{-4}	1.25×10^{-2}	--
Sb	1.0×10^{-5}	4.8×10^{-8}	2.5×10^{-4}	3×10^{-4}	1.75×10^{-2}	--
La	9.3×10^{-4}	2.8×10^{-8}	6.0×10^{-4}	7×10^{-4}	3.1×10^{-5}	--
Ce	1.2×10^{-3}	3.8×10^{-8}	1.2×10^{-3}	6×10^{-4}	1.3×10^{-4}	--
Th	1.4×10^{-4}	4.8×10^{-9}	2.0×10^{-4}	7×10^{-5}	1.5×10^{-5}	--
Pb	1.9×10^{-4}	2.8×10^{-9}	4.0×10^{-3}	1.7×10^{-2}	6.75×10^{-1}	≈ 1.0

Source: Kowalczyk et. al (Reference 17)

* Total Suspended Particulate

Table 7. Source Composition Data - Medford, Oregon (a)
(weight percent of mass)

Specie	Transportation(c) Fine Mode(b)	Soil Dust Coarse Mode(b)	Marine Aerosol Coarse Mode(b)	Calcium Source Coarse Mode(b)
Organic C	31.24	3.70	-	4.50
Elemental C	31.02	0.70	-	3.60
Total C	62.26	4.40	-	8.10
NO ₃	12.60	-	-	0.0
SO ₄	1.49	0.06	10.00	0.93
Na	-	1.70	40.00	0.43
Mg	0.25	1.50	4.80	1.25
Al	0.06	8.90	-	0.86
Si	0.25	27.00	-	2.90
S	1.53	0.07	3.30	0.54
Cl	1.53	-	40.00	0.96
K	-	0.75	1.40	0.48
Ca	0.69	1.80	1.40	25.80
Ti	0.13	0.70	-	0.0
V	-	0.03	-	0.0
Cr	-	0.02	-	0.0
Mn	-	0.18	-	0.03
Fe	0.53	5.50	-	0.33
Ni	-	0.0	-	0.02
Cu	-	0.03	-	0.04
Zn	0.28	0.01	-	0.0
Br	3.44	-	0.20	0.0
Pb	8.89	-	-	0.0

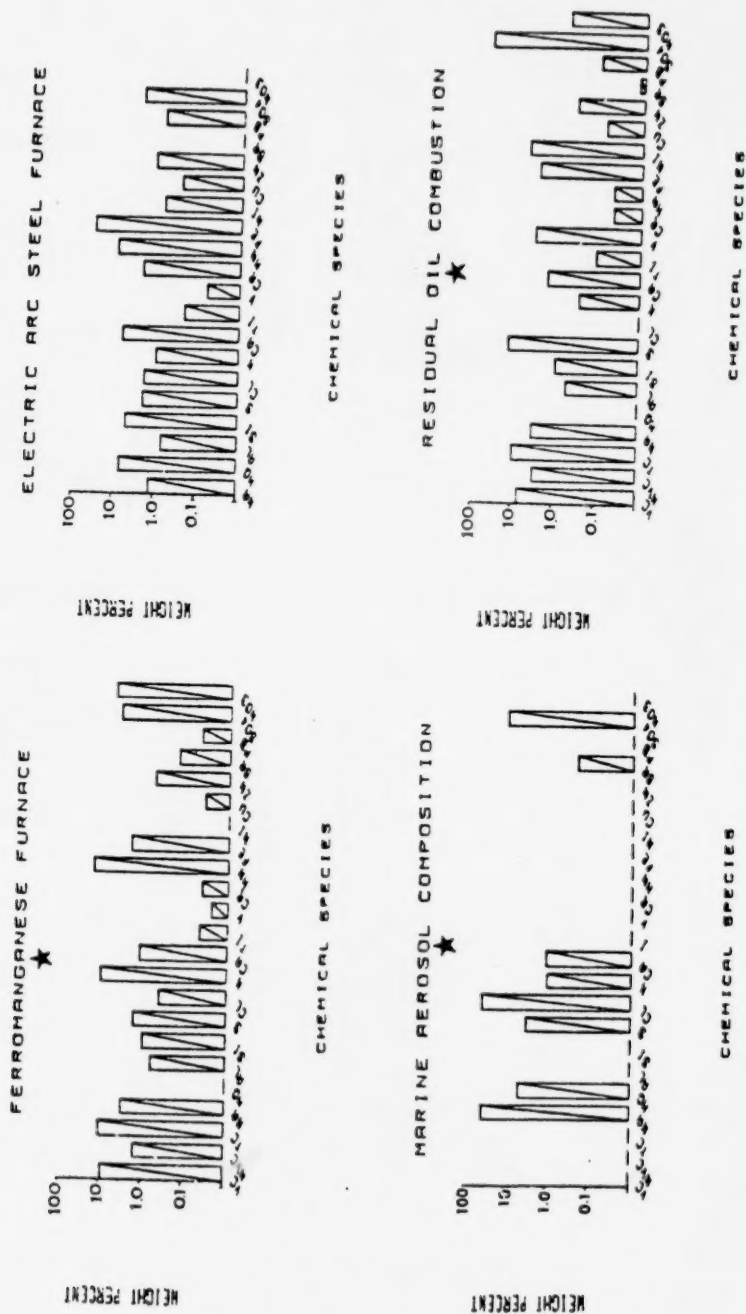
(a) Partial listing

(b) Fine Mode <2.5µm, Coarse Mode 2.5-20µm

(c) Represents a weighted average of diesel, leaded and unleaded emissions

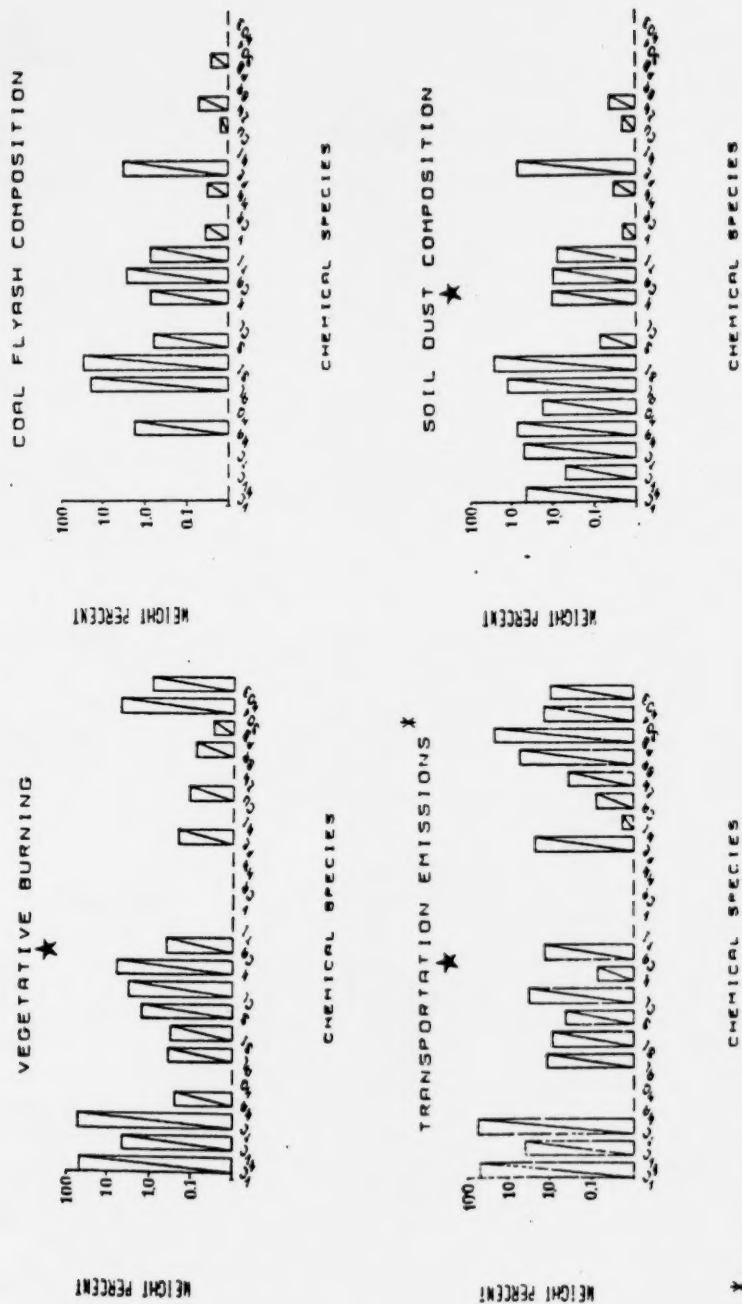
SOURCE: DeCesar and Cooper (Reference 22)

Figure 4
Source Composition Patterns
(Fine Particle Mode)



★ see text, page 32

Figure 4 (continued)
Source Composition Patterns
(Fine Particle Mode)



* PORTLAND, OR. 1978

* see text, page 32

sources characterized during the Portland Aerosol Characterization program and other studies. Because of the similarity in composition between soil, rock crusher and asphalt production emissions, only soil dust composition was used in the analysis as a surrogate for all three source classes. The source composition data presented in the tables and figures included in this section should only be used in other studies after careful review of the original documentation in relation to the nature of the sources under study.

3.0 PRINCIPLES OF CHEMICAL MASS BALANCE

The theoretical basis, input requirements and means for interpretation of CMB results are presented in this chapter. The Chemical Mass Balance method has evolved from concepts originally suggested in the early 1970's by M. S. Miller, S. K. Friedlander and G. M. Hidy¹³⁻¹⁵ to assess the impact of automotive exhaust and soils using lead and silicon as chemical tracers. Persons interested in applying these methods should be aware that inconsistencies in the notation, approaches to the use of fitting elements, solutions to the CMB equation, and source composition assumptions have resulted from the rapid growth of the technology. Potential users should therefore expect to encounter inconsistencies in the literature.

The starting point for the Chemical Mass Balance Model is essentially the same as the source (dispersion) model. The source model states that the contribution of a source to a receptor is dependent upon the emission rate and a dispersion factor. Limitations of dispersion modeling, however, arise from difficulty in quantifying dispersion factors in areas of complex terrain and/or meteorology, from difficulties in identifying emission rates, and other operating parameters associated with emission sources. The advantage of the CMB, and other receptor approaches, is that an exact knowledge of these parameters is unnecessary.

3.1 Model Theory

The basic assumptions inherent in the CMB approach are essentially the same as those associated with other receptor and source (dispersion) models²⁵:

° The particulate mass measured at the receptor is a direct, linear sum of the mass contribution from a number of specific sources

$$m = \sum_{j=1}^p M_j \quad (1)$$

where

m = measured concentrations of particles from all "p" sources ($\mu\text{g}/\text{m}^3$)

M_j = the impact at the receptor of source "j" ($\mu\text{g}/\text{m}^3$)

Similarly, the concentration of a given chemical species is assumed to be the sum of the contributions from each individual source emitting that species.

$$C'_i = \sum_{j=1}^p F_{ij}' X_{ij} M_j \quad (2)$$

where

C'_i = measured concentration of species "i" from all sources "p" ($\mu\text{g}/\text{m}^3$)

F_{ij}' = the fraction of species "i" in the emissions of source "j" as measured at the source

X_{ij} = the coefficient of fractionation of species "i" in the emissions of source "j." Fractionation is a systematic change in relative species abundances as the aerosol ages due, for example, to gravitational settling or condensation of volatile organic hydrocarbons

M_j = the impact at the receptor of source "j" ($\mu\text{g}/\text{m}^3$)

The F_{ij}' values associated with major emission sources are measured or adapted from literature values, and the C_i data are obtained through field monitoring programs. One can ensure a fractionation coefficient which approaches unity by (a) using stack gas dilution techniques to ensure capture of condensible aerosols and (b) obtaining size-resolved source composition and ambient aerosol measurements. By conducting fine and coarse mode CMB calculations, source

composition (F_{ij}') errors due to gravitational settling of large particles can be minimized. If no further fractionation or source emission composition changes are assumed to occur, then X_{ij} is assigned a value of unity and F_{ij}' can be considered to remain unchanged in time and distance downwind when measured at the receptor ($F_{ij}' = F_{ij}$).

By dividing both sides of equation (2) by the particulate mass collected at the receptor, all of the variables in the equation are expressed as a ratio to the aerosol mass:

$$C_i = \sum_{j=1}^p F_{ij} S_j \quad (i=1 \text{ to } n) \quad (3)$$

where

C_i = concentration of species "i" expressed as a ratio to mass (i.e., $C_i = C_i' / \sum_{j=1}^p M_j$)

F_{ij} = the fraction of species "i" in the emissions from source "j" at the receptor, expressed as a ratio to mass

S_j = the impact at the receptor of source "j" expressed as a ratio to mass emitted from all sources impacting the receptor (i.e., $S_j = M_j / \sum_{j=1}^p M_j$)

n = the number of chemical species considered

p = the number of sources impacting the receptor.

Since S_j is the quantity to be determined, a set of simultaneous equations can be written for all "p" sources of species "i," where "i" is defined as a "fitting" element.

Example Case

An appropriate example of Chemical Mass Balance principles might be the apportionment of soil dust, electric arc furnace steel emission, and auto exhaust within an Air Quality Maintenance Area exceeding particulate standards. Coarse mode ambient aerosol measurements taken in the area provide information on iron (Fe), silicon (Si), aluminum (Al), and lead (Pb), species known to be associated with the major emission sources. Source composition (F_{ij}) data for the major emission sources have either been obtained through test of local sources, adapted from the literature or both. Equation (1) in this case, is equivalent to the statement:

$$m = M_{\text{soils}} + M_{\text{steel}} + M_{\text{auto}} \quad (1A)$$

where

m = the mass concentration of aerosol ($\mu\text{g}/\text{m}^3$)

M_{soils} = the impact at the receptor of soil dust ($\mu\text{g}/\text{m}^3$)

M_{steel} = the impact at the receptor of steel emissions ($\mu\text{g}/\text{m}^3$)

M_{auto} = the impact at the receptor of auto exhaust ($\mu\text{g}/\text{m}^3$)

Equation (3A) describes the relationship between the measured concentrations of the chemical species in the ambient air to those of the sources. Iron (Fe) is used in the following example. The ambient concentration (C_i) is assigned a value of $0.2 \mu\text{g}/\text{m}^3$ of Fe, the particulate mass measured is $100 \mu\text{g}/\text{m}^3$ and the source composition values (F_{ij}) for soils, steel and auto exhaust are taken from Table 5 (coarse). The fractionation coefficient (X_{ij}) is assumed to be 1.0.

<u>Source</u>	<u>Coarse Mode Composition, $F_{Fe,j}$</u>
soils (urban dust)	5.73%
steel	32.0%
auto	2.1%

$$0.2 \text{ } \mu\text{g}/\text{m}^3 = (.0573 \frac{M_{j\text{soil}}}{100}) + (.320 \frac{M_{j\text{steel}}}{100}) + (.021 \frac{M_{j\text{auto}}}{100}) \quad (3A)$$

where

M_j is the source impact at the receptor

Fitting elements are those species known to be associated with the sources being considered. They are selected by reviewing the source composition data. Table 5 indicates that a good, nearly unique, fitting element for auto exhaust is lead (Pb), while steel and soil dust are primarily composed of Na, Mg, Al, Si, K, Ca, Ti, and Fe. The philosophy of selecting "fitting" species varies among investigators. Some prefer to use only a few elements (typically Fe, Al) for soils, while others opt for using a maximum number of species (Fe, Al, Si, Ca, and Ti) on the premise that the model's sensitivity to laboratory analytical error is minimized by including many species in the fit.

Once the fitting elements are selected, a set of simultaneous equations (3A) is created. In our example, soils, steel industry and auto exhaust emissions are believed to be the major sources in the coarse fraction, so Fe, Al, Si and Pb are used as fitting elements:

$$\begin{aligned}
C_{Fe} &= \sum_{j=1}^P F_{Fe, \text{soil}} S_{\text{soil}} + F_{Fe, \text{steel}} S_{\text{steel}} + F_{Fe, \text{auto}} S_{\text{auto}} \\
C_{Al} &= \sum_{j=1}^P F_{Al, \text{soil}} S_{\text{soil}} + F_{Al, \text{steel}} S_{\text{steel}} + F_{Al, \text{auto}} S_{\text{auto}} \\
C_{Si} &= \sum_{j=1}^P F_{Si, \text{soil}} S_{\text{soil}} + F_{Si, \text{steel}} S_{\text{steel}} + F_{Si, \text{auto}} S_{\text{auto}} \\
C_{Pb} &= \sum_{j=1}^P F_{Pb, \text{soil}} S_{\text{soil}} + F_{Pb, \text{steel}} S_{\text{steel}} + F_{Pb, \text{auto}} S_{\text{auto}}
\end{aligned} \tag{3A}$$

where:

° C_{Fe} , C_{Al} , C_{Si} , and C_{Pb} are ambient concentrations of Fe, Al, Si and Pb ($\mu\text{g}/\text{m}^3$)

° $F_{Fe, \text{soil}}$; $F_{Al, \text{steel}}$; $F_{Si, \text{auto}}$, etc. are source composition estimates (see Table 5, coarse mode).

This set of equations is usually solved by linear least squares or effective variance solutions using commonly available matrix mathematics. Sections 3.1.1 through 3.1.3 describe the solutions to these equations further.

If, for example, the iron content in soil dust is assumed to be unchanged downwind of its source ($F'_{Fe, \text{soil}} = F_{Fe, \text{soil}}$), and both sides of equation (3A) are divided by the particulate mass ($100 \mu\text{g}/\text{m}^3$), the following statement can be made. Note that the quantity ($\frac{M_i}{100}$) has been redefined as S_j :

$$\frac{0.2 \mu\text{g}/\text{m}^3}{100 \mu\text{g}/\text{m}^3} = (.0573 S_{j\text{soil}}) + (.320 S_{j\text{steel}}) + (.021 S_{j\text{auto}})$$

Since we are interested in solving this equation for the S_j values associated with soils, steel and auto emissions, a set of simultaneous equations now needs to be developed. Each of "fitting" species noted in equation (3A) are included below. As before, source composition data is taken from Table 5, coarse mode. Ambient concentrations of coarse mode Fe, Al, Si, and Pb are taken as 0.2, 0.6, 1.8, and 1.2 $\mu\text{g}/\text{m}^3$ respectively.

$$0.2 \mu\text{g}/\text{m}^3 \text{ Fe} = (.057 S_{\text{soil}}) + (.320 S_{\text{steel}}) + (.021 S_{\text{auto}})$$

$$0.6 \mu\text{g}/\text{m}^3 \text{ Al} = (.066 S_{\text{soil}}) + (.006 S_{\text{steel}}) + (.001 S_{\text{auto}})$$

$$1.8 \mu\text{g}/\text{m}^3 \text{ Si} = (.280 S_{\text{soil}}) + (.050 S_{\text{steel}}) + (.008 S_{\text{auto}})$$

$$1.2 \mu\text{g}/\text{m}^3 \text{ Pb} = (.003 S_{\text{soil}}) + (.007 S_{\text{steel}}) + (.200 S_{\text{auto}})$$

Solutions to this set of equations are presented in Sections 3.1.1 through 3.1.3. Once S_{soil} , S_{steel} and S_{auto} are determined, they are multiplied by 100 to obtain the percent contributions of soils, steel and auto exhaust to the measured aerosol mass concentration.

3.1.1 Tracer Property Solution

Perhaps the simplest way to solve the set (3) of equations is to use the tracer method. This method assumes that each source type has a unique property (element or compound) which is found in no other source category. If this is true, then equation 3 can be reduced to:

$$C_i = F_{ij} S_j \text{ or } S_j = \frac{C_i}{F_{ij}} \quad (4)$$

where the impact of source j (S_j) can be determined by dividing the concentration of tracer element "i" (C_i) by the fraction of tracer element "i" in the sources' emissions (F_{ij}). For example, if (a) fine particulate Pb is considered as a

unique tracer for leaded auto exhaust, (b) an assumed concentration of Pb as 20% of the total emission mass for automobiles, and (c) $1.0 \mu\text{g}/\text{m}^3$ of Pb is measured at the receptor, the total impact of leaded auto exhaust is $5 \mu\text{g}/\text{m}^3$ ($1.0 \mu\text{g}/\text{m}^3 \div 0.20$). This approach can be extended to other sources so long as the tracers meet the following requirements:

- ° the fraction of the tracer in the source emission is invariant with time
- ° the concentration of the trace element can be accurately and precisely measured in the ambient sample
- ° the tracer element is emitted by only one source category.

These conditions are difficult to meet, are highly susceptible to analytical and sampling errors in both the ambient and source particulate and tend to ignore useful information contained in the ambient aerosol "fingerprint."

Slight variations of the tracer approach have, however, been used as semiquantitative estimates of source impacts. Fine particle K/Fe ratio information used in association with data on the fraction of potassium in smoke can be thought of as a CMB tracer-mode approach to vegetative burning impact assessment in which fine particle mode potassium is used as a tracer.³

3.1.2 Linear Least Squares Solution

The set of equations (3 above) is most often solved for the S_j values by a number of more complex mathematical procedures, all of which use standard matrix manipulation techniques. The basic approach consists of an ordinary linear least squares solution to the set of simultaneous equations.²⁶ This

approach is based on the principle of a least squares regression first published by Friedlander.¹³ The method attempts to find a combination of S_j 's that minimize the sum of the squares in the deviation between the measured and predicted specie concentrations designated as fitting elements.²³ The least squares solution requires that there be more fitting elements than S_j 's to be determined [i.e., more equations than terms in equation set (3)]. Once the S_j 's are determined, however, all of the specie contributions from each source and the total predicted concentration of each specie can be computed and expressed as a ratio to the measured specie concentration as a measure of the quality of fit. Estimated concentrations of species not designated as "fitting" components (referred to as "floating" elements) can be used as independent measures of the adequacy of the "fit." Although the ratio of the calculated/measured specie concentrations should ideally be "1.0," researchers usually consider ratio values within a range of 0.5 to 2.0 to be acceptable.

Improvements to the ordinary least squares approach have been suggested by Kowalczyk and co-workers.²⁷ These investigations have concluded that unweighted least squares fitting procedures are unsatisfactory, since they tend to ignore important species (i.e., As, Mn) that are often found in concentrations near the minimum detection limit of the analytical methods used. To properly account for these less abundant species in the fitting process, a weighted least square solution based on the inverse of the absolute standard deviation (of a single determination) of the measured atmospheric concentration has been used. This procedure gave excellent fits to concentrations of fitting elements in studies of Washington, DC aerosol. Further, the procedure allows one to propagate the uncertainties in the ambient aerosol specie measurements through the calculation to define the confidence interval around the calculated source impact (S_j).

3.1.3 Effective Variance Least Squares Fitting

Watson²³ recognized the need to weight the least squares solution in accordance with uncertainties in both the source composition (F_{ij}) and the ambient aerosol species (C_i). Such a procedure ensures that those components with the greatest uncertainties received less weight in the fit and that both sources of uncertainties are propagated through to the source impact (S_j) determination. The method involves minimizing the function:

$$\chi^2 = \sum_{i=1}^n \left\{ \frac{[C_i - \sum_{j=1}^P F_{ij} S_j]^2}{\sigma^2 C_i + \sum_{j=1}^P \sigma^2 F_{ij} S_j^2} \right\} \quad (6)$$

where:

$\sigma^2 C_i$ is the variance or uncertainty in the concentration of species i in the ambient aerosol

$\sigma^2 F_{ij}$ is the variance or uncertainty in the fraction of species i in the emissions from source j

Conceptually, the numerator of the function represents the difference between the measured and CMB-predicted specie concentrations, while the denominator is the variance of that difference achieved by the propagation of uncorrelated, normally distributed precisions in the measurements. The minimization is accomplished by setting the partial derivatives of χ^2 with respect to each S_j to zero and solving for the S_j 's. The resulting equations are non-linear and are solved by an iterative method.

Of equal importance to the proper weighting of the species in the fitting process, is the fact that the CMB estimated source strengths obtained by this scheme are accompanied by estimates of likely associated error. Source impact uncertainties listed in Table 8 were derived thru minimizing the effective variance as described above. Much work needs to be done, however, to better assess the uncertainties in the chemical composition of source emissions.

Figure 5 illustrates the principles of the chemical mass balance approach, using example sources described above. In practice, it would be beneficial to extend equation 3 to include a fifth term (Br) to serve as a second tracer for leaded auto exhaust and thereby help assign that portion of the Fe, Al and Si associated with leaded auto exhaust.

Perhaps a clearer perception of the CMB fitting procedure is gained by matching the ambient fingerprints shown in Figure 3 (page 8) with the source "fingerprints" shown in Figure 4. The reader may wish to draw the figures marked with a star (★) onto a transparent medium and attempt to match them as described below. The January 27, 1978 downtown Portland (midnight to 4 a.m.) pattern will be used in the following example.

An examination of the elemental ratios in this sample compared to the source composition patterns suggest that only the ferromanganese furnace emission have the high Mn/Fe ratio found in the ambient sample. If a "best fit" between these two patterns is attempted (e.g., the Na, K, Ca, and Fe lines are matched in height), we find that additional sources of Al, Si, S, Cl, V, Ca, Ni, Cu, Zn, Br, and Pb are needed to explain the aerosol composition.

Table 8. CMB-Estimated Source Contributions
Downtown Portland, Oregon - Fine Fraction, January 28, 1978
(Midnight to 4 a.m.)

<u>Source</u>	<u>$\mu\text{g}/\text{m}^3$</u>	<u>% of mass</u>
Marine Air	.31 + .19	0.82 + 0.5
Urban Dust	.69 + .28	1.81 + 0.7
Auto Exhaust	1.17 + .19	3.0 + 0.5
Residual Oil Comb.	1.65 + .27	4.3 + 0.7
Vegetative Burning	7.54 + 3.2	19.7 + 8.5
Ferromanganese Furnace	6.46 + .57	16.9 + 1.6
Nitrate	.65 + .32	1.7 + 0.8
Sulfate	8.31 + 1.41	21.8 + 3.8
Total	26.80 + 3.60	70.0 + 10.4

<u>Specie</u>	<u>Measured ($\mu\text{g}/\text{m}^3$)</u>	<u>Calculated ($\mu\text{g}/\text{m}^3$)</u>	<u>Ratio (calc/meas)</u>
NO ₃	1.197	1.197	1.00
SO ₄	9.805	9.805	1.00
Na	0.416	0.417	1.002
Al	0.149	0.158	1.062
Si	0.277	0.281	1.014
S	2.937	3.236	1.102
Cl	1.024	0.934	0.914
K	1.520	1.185	0.780
Ca	0.151	0.215	1.428
Ti	0.012	0.015	1.227
V	0.063	0.059	0.937
Cr	0.054	0.005	0.086
Mn	1.101	1.123	1.028
Fe	0.449	0.255	0.569
Ni	0.080	0.089	1.116
Cu	0.028	0.009	0.308
Zn	0.371	0.049	0.132
Br	0.064	0.074	1.158
Pb	0.247	0.243	0.982

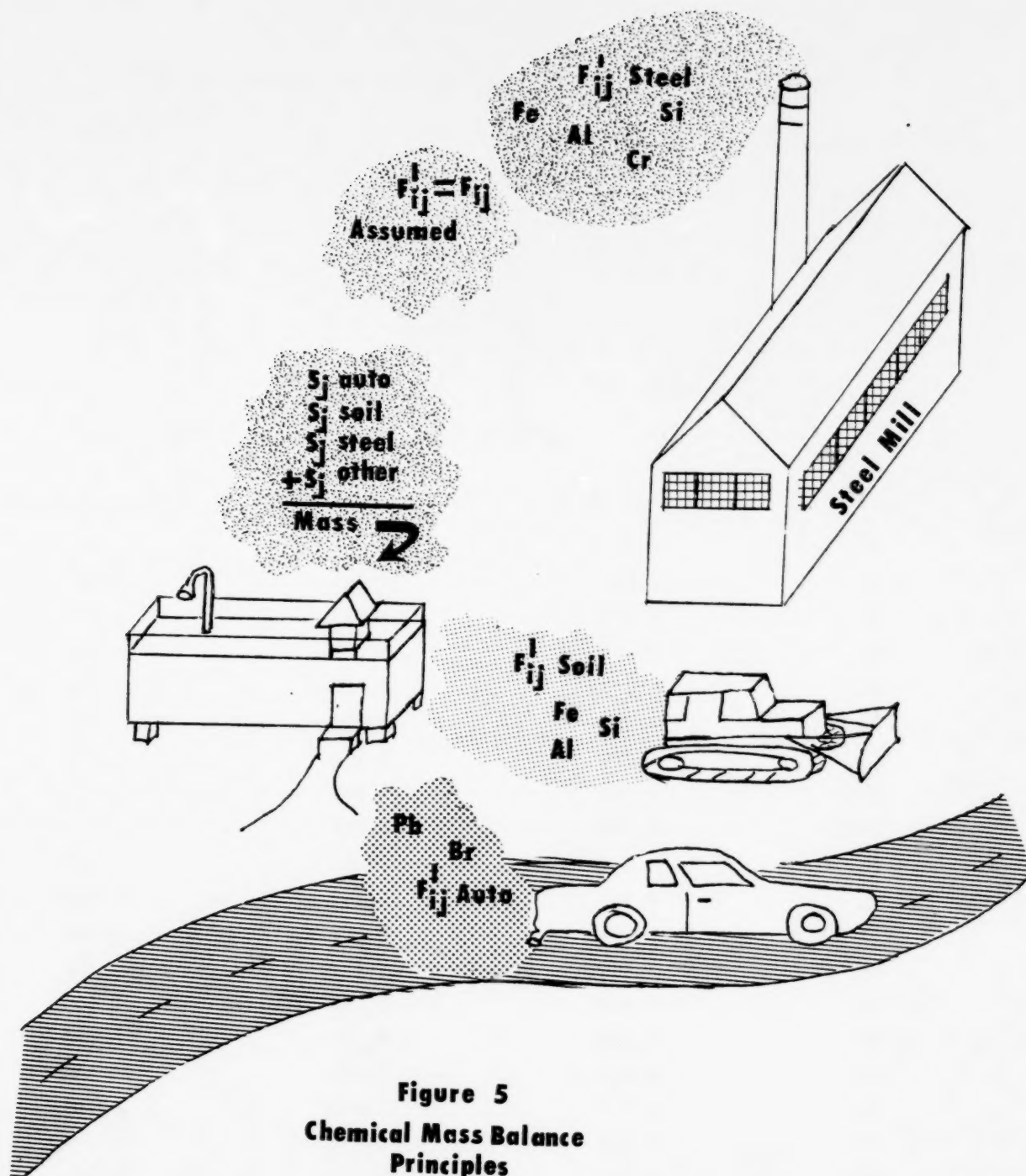


Figure 5
Chemical Mass Balance
Principles

Since we know from Table 5 (page 15) that residual oil combustion is a main source of Ni and V in Portland, the source fingerprint for this source can be added. Using Ni and V as "fitting" elements, the residual oil pattern is fit to the ambient pattern such that the Ni and V lines match one another.

Among the remaining elements, Br and Pb can be accounted for by adding the auto exhaust pattern to the fit using Br and Pb as fitting elements. Soil dust accounts for the Al and Si concentrations and marine air is used to fit Na and Cl. Vegetative burning is used to match the remaining C, K and Cl. The sources of Cu and Zn were not directly identified in the Portland study but may be associated at least in part, with hi-vol sampler armature wear and galvanizing operation, respectively. The remaining S was assigned to secondary sulfate.

The CMB model completes the above process mathematically to insure the best "fit" between the source and ambient aerosol "fingerprint" (or species ratios). Table 8 is the CMB model output for the above example and includes several species not included in the figures. Seventy percent of the mass was accounted for, although only 30% of the Cu and 13% of the Zn were identified.

3.2 Model Input Requirements

The input data required for the CMB model consists of (a) the concentrations of chemical species of which the ambient aerosol is composed (C_i), (b) the sources which are likely contributors to the aerosol measured at the receptor, and (c) the source composition (F_{ij}) of each source's emissions. While the development of the required input data is not simple, considerable progress has recently been made in the chemical characterization of ambient particulate matter and source emissions such that much usable information is already available

for many communities. Chapters 4 and 5 of this document describe the characteristics of ambient and source particles in greater detail.

3.2.1 Ambient Aerosol Data Requirements

Ideally, the chemical composition of the ambient aerosol should be characterized for both the fine (0.1-2.5 μm) and coarse (2.5-10 μm) modes. Sample analysis should be conducted for each of the major components which collectively account for the total mass of the aerosol. By completely characterizing the aerosol in this way (a) the CMB predicted mass can be compared to the measured mass as an indicator of the quality of the source apportionment fit, (b) the ability of the model predictions to account for important species is more readily apparent, and (c) a greater proportion of the ambient aerosol mass can be explained. Table 9 lists species that, at a minimum, should be included in ambient (and source characterization) measurements intended for input to the model.

Table 9

CMB Model Ambient and Source Characterization
Measurement Input Requirements
(size resolved samples preferred)

mass	Cl	Fe	Pb
Na	K	Ni	SO ₄
Mg	Ca	Cu	NO ₃
Al	V	Se	Organic Carbon*
Si	Cr	Br	Elemental Carbon*
S	Mn	Ba	
As	Sr	Cd	
Sn	Sb		

* See text below

Organic and elemental carbon²⁸ are "operational" definitions related to the specific analytical method employed. In general, organic carbon is that portion of the ambient carbon aerosol that is oxidized to carbon dioxide when heated in an oxygen-free atmosphere at a temperature of about 600°C. Elemental carbon is the remaining material oxidized to CO₂ when the sample is heated in a helium-oxygen atmosphere. Since some of the organic carbon may be converted to elemental carbon during sample analysis, data compatibility is dependent on the use of similar analytical techniques. Measurement of the organic and elemental carbon have proven extremely useful in apportioning carbon sources (wood burning, diesel exhaust, distillate oil, etc.)²⁰

It is possible, however, to perform chemical mass balance analysis using only total particulate samples and elemental composition data. The success of this approach, however, is limited to airsheds in which the source emissions are "element-rich" with few carbonaceous sources. In applications where this approach is suitable, size segregated samples analyzed for elemental content as part of the EPA Inhalable Particulate Network will provide a great deal of usable data for CMB analysis. Additional analysis of these filters for ions and carbon (using nuclear methods) would provide an excellent data base for CMB use.

If an effective variance CMB model is to be used, the precision of the analytical measurements must be known. Since the precision of the measurements will vary among laboratories, between and within methods, and by species, it is important that laboratories conducting analysis for CMB purposes provide the user with precision estimates associated with each sample analyzed.

3.2.2 Source Characterization Input Requirements

The source composition input data needs require that the major source categories impacting the receptor be identified and that their emissions be chemically characterized. Sources likely to impact the receptor are determined by emission inventories of the airshed, likely upwind sources not included in the inventory, and non-inventoried sources that may be contributors. Once identified, the chemical composition of the emissions (in the fine and coarse modes) are measured by source testing or obtained through a literature review of similar sources. The variability of the composition of the emissions for each source over time should ideally be determined through multiple tests to provide an uncertainty estimate (standard deviation of each specie) if the effective variance CMB model is to be used. In practice, several source samples are obtained during a single sampling session. Results are then analyzed and the standard deviation of the data set is calculated for each species.

Although the volume and general adequacy of source emission characterization data useful for CMB proposed is very limited, several studies have been completed which rely almost entirely on data reported in the literature. Future EPA programs aimed at characterizing fine and coarse particle emission will greatly improve and expand the current data base.

3.3 Interpretation of CMB Results

The interpretation of CMB results plays an important role in the use of the technique. Unfortunately, errors in model assumptions, source emission chemistry, element volatility, analytical limitations, and other factors provide CMB results which must be interpreted by the investigator. Source contributions identified by the model tell us which source combinations could reproduce the ambient

aerosol fingerprints measured, but not necessarily which sources actually did influence the receptor. Because many of the source fingerprints are in reality representative of a source class, it is often impossible to distinguish which specific source within the source class impacted the receptor without supportive information.

A typical problem in interpreting CMB results arises from the fact that, in reality, the model identifies chemical "fingerprints" rather than specific sources. Examples of potential pitfalls in interpreting CMB results which have been encountered in past applications follow.

° Vegetative burning emissions from fireplaces, wood stoves, and land clearing were found to be so similar to one another that they were grouped together as a single source class. Since these emissions are largely found in the fine particle mode, CMB results which identified large burning impacts in the coarse mode were unexpected. Further investigation, however, revealed that the composition of unburned plant tissue (pollen, grass, etc.) was sufficiently similar to that of the smoke resulting from the burning that the two could not be distinguished by CMB. Distinctions between vegetative burning (smoke) emissions and unburned plant tissue were therefore found to be highly dependent on particle size.

° Fugitive emissions of coarse mode particulate rich in calcium, although often labelled as cement dust, may represent impacts from any of a number of sources including crustal limestone, building demolition, calcium carbide furnace process losses, agricultural lime processing and application, cement pavement attrition, calcium sulfate fertilizer dust, or any other calcium

source. Further efforts to apportion calcium sources must be based on supplemental information about likely emissions within the airshed, source activities, and transport.

° Most importantly, definitive evaluation of CMB results can only be obtained by having a good estimate of the quality of the ambient and source characterization data, the degree of uncertainty in the measurements, the ability of the model to predict measured species (and mass), and the interaction of the sources in the CMB fitting process. Watson²³ found numerous interactions between "single constituent" sources (such as secondary sulfate) and other sources included in the fit. Watson's algorithm assigned all sulfate not accounted for by other sources to the secondary sulfate category, thereby "using up" all of the sulfate component. To avoid biasing the fitting process, "single component" sources, such as secondary sulfate and nitrate, were only included in the CMB fit after other sources had been tried. Other fitting interactions between Kraft recovery furnace emissions and marine aerosol used in association with secondary sulfate produced nearly identical fits.

These examples of potential CMB interpretation "pitfalls" are included to emphasize the importance of understanding not only the quality of input data and fitting process, but to highlight the need for evaluation of model results (Chapter 6.0).

3.4 Emission Inventory Scaling

Emission inventory scaling techniques can occasionally be used in association with other source apportionment methods to identify the impact of an unknown source. If, for example, chemical mass balance methods can identify the impact

of a residual oil-fired boiler located adjacent to a distillate-oil fired boiler stack, the impact from the distillate fuel combustion can reasonably be assumed to be in the same proportion as the emission rate of the two boilers if (a) the plume height and dispersion characteristics are similar, (b) the operating schedule for both sources is identical, and (c) the particle size distribution and deposition rates of the emission are the same.

This approach is occasionally used to identify the impact of diesel truck emissions. Given the impact from leaded automotive exhaust (often based on a Pb tracer) and the inventory ratio of diesel/leaded exhaust emission, the impact of diesel emissions can be calculated if the diesel and automotive emissions are assumed to be spatially and temporally similar. This may, or may not, be defensible based on the location of the sampling sites to nearby roadways and the local traffic mix.

3.5 Chemical Mass Balance Computer Software

Application of the Chemical Mass Balance model requires a computer facility of sufficient size to store the source composition and ambient particulate data, the computation program and output files. Both interactive and batch process programs are currently in use at State regulatory agencies, EPA, universities, consultants, and within industry. As noted earlier, the least square solutions to the set of simultaneous equations requires standard matrix inversion, addition, subtraction, and multiplication routines that are commonly available on larger computer systems. The availabilities of these software routines and limitations on computation speed are two reasons that the software has not yet been adapted to micro-computers. Since the memory requirements of the program are largely dictated by the size of the matrix (typically 10 sources x 20 chemical species in

dimension), computational requirements are minimal and CMB programs are very inexpensive to run. Due to the continuing development of the CMB technique and need to complete CMB model validation studies, no single set of standard software currently exists. Professionals currently using these programs have either developed them internally, borrowed or purchased them from other users.

As an example of the computation process and criteria used in a CMB analysis, an interactive program developed and documented by Watson²³ will be discussed. The code allows the operator to specify the initial sources and species to be included in the calculation, performs either ordinary weighted least squares or effective variance fitting schemes as selected by the operator and computes a reduced chi-square statistic as a measure of the goodness of the overall "fit" between the measured and CMB-predicted specie concentration. The program then writes the results out to the operator's terminal in the format shown in Table 10. The best "fit" is then obtained by adding or deleting sources in accordance with the following criteria:

- ° the estimated to measured mass ratio should approach, but not significantly exceed 1.0;

- ° the predicted/observed specie concentrations for most elements should be within the range of 0.5 to 2.0;

- ° the estimated source contribution should be greater than its associated uncertainty.

Following these criteria and given knowledge of the source's composition within the study area, the operator can add sources rich in species seen to be

Table 10. CMB Model Output -- Format

```

FINE SITE: CANS DATE: 780127 SAMPLE DURATION: 24 W/ START HOUR: 0
REDUCED CHI: .887 DF: 7
1 MACHINE * .361+- .215 UG/M3
2 CRUST * .700+- .214 UG/M3
3 TRANSP * 1.132+- .192 UG/M3
5 RESOIL * 1.642+- .271 UG/M3
8 VBURN2 * 14.856+- 5.461 UG/M3
10 FERRO * 6.301+- .570 UG/M3
12 SECNO3 * .692+- .281 UG/M3
13 SECNO4 * 7.994+- 1.314 UG/M3
TOTAL: 32.877
MEASURED MASS FINE/COARSE/TOTAL:
38.100+- 1.500/ 46.300+- 3.176/ 86.400+- 2.800
PRESS TRANSMIT TO CONTINUE OR ENTER C FOR NEXT COMMAND
*****MEAS*****CALC*****RATIO*****
1 VC * < .001 7.937+- 1.344 .00+- .00 VC
2 NA * .416+- .058 .439+- .060 1.06+- .21 NA
3 TC * < .001 8.189+- 1.768 .00+- .00 TC
4 K * 1.520+- .120 1.519+- .429 .99+- .29 K
5 MG * < .540 .026+- .257 26.40+-***** MG
6 S * 2.937+- .240 .555+- .108 .19+- .04 S
7 SO4 * 9.815+- 1.037 9.815+- .751 1.00+- .13 SO4
8 NO3 * 1.197+- .166 1.197+- .220 1.00+- .23 NO3
9 NVC * < .001 .725+- .425 .00+- .00 NVC
10 NH4 * < .001 .000+- .000 .00+- .00 NH4
11 CL * 1.024+- .103 .640+- .284 .63+- .28 CL
12 F * < .001 .019+- .005 .00+- .00 F
13 AL * .149+- .020 .171+- .047 1.15+- .35 AL
14 SI * .277+- .030 .286+- .036 1.03+- .17 SI
15 CA * .151+- .014 .200+- .045 1.33+- .32 CA
16 TI * .012+- .003 .009+- .002 .77+- .23 TI
17 V * .063+- .004 .058+- .012 .92+- .21 V
18 CR * .054+- .005 .004+- .001 .08+- .02 CR
19 MN * 1.171+- .078 1.092+- .062 .99+- .09 MN
20 FE * .449+- .034 .275+- .123 .61+- .28 FE
21 NI * .030+- .007 .088+- .020 1.10+- .27 NI
22 CU * .028+- .004 .020+- .056 .71+-2.01 CU
23 Zn * .371+- .038 .048+- .016 .13+- .05 Zn
24 BR * .064+- .006 .079+- .026 1.23+- .42 BR
25 PB * .247+- .022 .233+- .034 .96+- .16 PB

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deficient in the initial calculation or delete sources which overpredict the measured specie concentration. The program is designed to perform CMB's on fine and coarse mode particulate fractions separately and sum the results, providing source impact estimates for three size fractions.

3.6 Status of Current Technology

Although the CMB model and its application to particulate mass source apportionment is a new and rapidly growing technology, much work needs to be done before the technique will realize its full potential or become as widely applied as dispersion modeling. An expanded data base of source emission characterization data, comprehensive model validation studies, and software improvements are still needed. Nevertheless, the method is considered by many researchers to be of comparable (or superior) accuracy to dispersion model impact assessment methods.¹

New advances in CMB software have recently included error propagation subroutines designed to provide an estimate of CMB-predicted source impact uncertainty based on likely errors in ambient aerosol measurements, and variations in source emissions. Table 11 summarizes source impact uncertainties calculated during the Portland Aerosol Characterization study. More information on source composition variations over time is needed to assess the accuracy of these estimates, however.

Chemical Mass Balance studies conducted in the State of Oregon and Washington, DC probably represent the current state of the art. These studies have been successful in apportioning the majority of the measured ambient mass concentrations into source and chemical classifications. Neither study, however,

Table 11. Typical Source Impact Uncertainties

Portland, Oregon Annual Average TSP²⁰

Source	Relative Uncertainty**	Source Impact % Annual Mean	% Uncert- ainty*	Source Im- pact $\mu\text{g}/\text{m}^3$	Uncertainty $\mu\text{g}/\text{m}^3$
Soil and Road Dust	$\pm 6\%$	39.0	$\pm .4$	24.8	± 1.5
Vegetative Burning	$\pm 17\%$	14.6	$\pm .5$	9.3	± 1.5
Auto Exhaust	$\pm 10\%$	9.2	$\pm .9$	5.8	± 0.6
Residual Oil Combustion	$\pm 10\%$	0.83	$\pm .08$	0.5	± 0.1
Aluminum Production	$\pm 22\%$	1.35	$\pm .3$	0.8	± 0.2
Steel Production	$\pm 14\%$	0.94	$\pm .13$	0.6	± 0.1
Marine Aerosol	$\pm 13\%$	3.8	$\pm .5$	2.4	± 0.3
Sulfite Re- covery Furnace	$\pm 6\%$	0.18	$\pm .01$	0.1	± 0.01
Ferromanga- nese Furnace	$\pm 38\%$	0.18	$\pm .07$	0.1	± 0.04

* Average uncertainty of single determination

** Uncertainty/source impact; relative uncertainties estimates are highly dependent on impact strength

has been able (through CMB analysis alone) to pinpoint single, specific source complexes unless they are unique within the airsheds. Identification of specific sources is usually accomplished by CMB impact estimates used in association with trajectory and source activity analysis. The Oregon and Washington, DC studies have also not been able to fully account for all of the Cu, Zn or Ca found in the ambient air, suggesting (a) errors in source composition data, or (b) that failure to characterize an important source. At least a portion of the unidentified Cu is undoubtedly associated with armature wear of hi-vol motors. Secondary aerosols, such as sulfates, which typically make up about one-half of the fine particle mass in many Eastern States are usually included in the mass balance analysis with no indication of their true origin. CMB can, however, help identify the likely origin of that portion of the sulfate fraction contributed as primary emissions from Kraft recovery furnaces, residual oil combustion, and other sources.

The current technology indicates that source apportionment studies based on Chemical Mass Balance can provide a wealth of information useful to State and local regulatory agencies during the control strategy development process. Scientifically defensible studies, however, must be designed, conducted, and results interpreted by professionals familiar with the limitations and proper use of the technique. Verification of CMB results, program quality assurance and comparisons with results from other techniques are highly important to overall program credibility.

4.0 SOURCE CHARACTERIZATION REQUIREMENTS

A brief description of the CMB model source characterization requirements as they relate to model input requirements is included in Section 3.2. This chapter focuses on the most critical, and difficult task related to CMB use; development of source "fingerprints" for the airshed under study. Application of values reported in the literature, and source testing program design are discussed.

4.1 Application of Values in the Literature

The use of literature values in CMB-oriented studies has been a common practice, largely because good information on source emission composition is difficult to obtain. Tables 4, 5, 6 and 7 (Section 2.2) summarize source composition data used in the St. Louis, Missouri, Portland, Oregon, Washington, DC, and Medford, Oregon programs.

Motor vehicle exhaust composition data taken from these tables can be used to illustrate the importance of understanding and interpreting values reported in the literature. Table 12 summarizes the exhaust composition data shown in Tables 4 through 7. Marked differences can be seen in the Br value (normalized in relation to lead) and in the absolute values of Pb, Zn, Ba, and carbon. Since Pb and Br are the primary fitting elements for motor vehicle exhaust, the use of appropriate values here is critical to the credibility of the CMB analysis.

A closer look at the research studies from which the data in Table 12 were taken, however, reveals that these data sets were intended to represent the chemical composition of a mixture of leaded, unleaded and diesel exhaust typical of the airshed at the time for which they were developed. Hence, the differences are largely a result of differences in the vehicle mix among the cities and the net change in lead emissions over time due to the phaseout of leaded gasoline.

Table 12. Motor Vehicle Exhaust Composition Summary From Literature Values

Specie	St. Louis, MO ^a % of Mass	Portland, OR ^b % of Mass	Washington, DC ^c % of Mass*	Medford, OR ^d % of Mass
Total Carbon	56.3 (3.80)**	53.8 (2.69)	-	62.26 (7.00)
Mg	0.6 (.04)	-	-	0.25 (.03)
Al	-	1.1 (.05)	-	0.06 (.01)
Si	-	0.82 (.04)	-	0.25 (.03)
P	0.09 (.006)	-	-	-
S	0.6 (.04)	0.4 (.02)	-	1.53 (.17)
SO ₄	-	1.3 (.06)	-	1.49 (.16)
Cl	1.9 (.12)	3.0 (.15)	1.0 (.10)	1.53 (.17)
K	-	0.72 (.36)	-	-
Ca	-	1.25 (.06)	0.5 (.05)	0.69 (.07)
Mn	0.06 (.004)	-	-	-
Fe	1.0 (.06)	2.1 (.10)	0.5 (.05)	0.53 (.05)
Ni	-	0.018 (0.0)	-	-
Cu	-	0.073 (.003)	-	-
Zn	3.0 (.20)	0.350 (.017)	0.15 (.015)	0.28 (.03)
Br	3.7 (.25)	5.00 (.25)	3.8 (.38)	3.44 (.38)
Ba	0.09 (.006)	-	0.13 (.013)	-
Pb	14.80 ($\pm$ 1.0)	20.00 ($\pm$ 1.0)	(10.0)*($\pm$ 1.0)	8.89 ($\pm$ 1.0)
NO ₃	-	0.91 (.045)	-	12.60 (1.41)
Total	82.1%	90.8%	16.1%	93.8%

* Based on a lead content of 10% assumed by Kowalczyk
 ** () normalized to lead content

- (a) Dzubay, Reference 24
- (b) Cooper, Reference 20
- (c) Kowalczyk, Reference 27
- (d) DeCesar, Reference 22

Dzubay's motor vehicle component is based on highway tunnel studies conducted by Pierson^{29,30} during the 1970-1973 period using hi-vol total particulate samples. Adjustments in Pierson's data were made by (a) assuming a vehicle mix of 96% gasoline powered light-duty motor vehicles and 4% diesel based on St. Louis transportation emissions data, and (b) adopting a Br/Pb ratio of 0.25 (rather than 0.39 for fresh exhaust) to account for instability in the bromine content of the aerosol.

Cooper's automotive component was developed by Watson²³ who, in turn, used Pierson's studies adjusted for bromine loss on the unleaded/leaded/diesel emission rates adjusted for the Portland, Oregon airshed in 1978.

Kowalczyk relied on work by Ondov³¹ conducted in 1974 in the Baltimore tunnel. The higher Br/Pb ratio suggest that the Br component has not been adjusted to reflect volatility losses while the lower lead content (10%) and higher Ba concentrations reflect the greater proportion of diesel emissions in the transportation mix when compared to Portland and St. Louis.

Cooper's Medford, Oregon 1980 transportation component is characterized by it's relatively low Pb content, high Br/Pb ratio, and high carbon content. Like the other transportation composites, this "fingerprint" reflects the diminishing proportion of lead due to the phase out of leaded fuels and the increased importance of diesel emissions in a community with a great deal of trucking activity. The composition data were developed from new studies of auto and diesel emissions by Wolff and Gorse,^{32,33} as well as from the earlier studies by Pierson.

These example cases illustrate potential pitfalls in accepting previously published source composition literature values for input to the CMB model. The specific form of the transportation "fingerprint" must be tuned to the nature of the emissions in the airshed under study. Major changes in source activities during the field study (e.g., a teamster's strike), the traffic mix or nearby roadways heavily impacting the receptor, the use of diesel fuel smoke suppression additives and nearby diesel train emissions are all factors that could effect the validity of the transportation "fingerprint." Accurate estimation of the Pb content is especially important in transportation impact analysis because it is the most commonly used (and most heavily weighted) fitting specie. Incorrect specification of the lead content by one-half of the true value will approximately double the predicted transportation impact.

Since the composition of emissions is often a function of particle size, care must be taken to specify the size fraction of the particles measured. Fine and coarse mode CMB input data should be used whenever possible to minimize errors associated with deposition of coarse particles (Section 3.1). Clear documentation of the source compositions used, assumption and weighting techniques used must be presented if the analysis is to be used for control strategy development purposes. While a detailed review of values reported in the literature is beyond the scope of this document, Table 13 lists, by source class, typical points that should be considered when using such data.

4.2 Source Testing Considerations

Source testing programs designed to capture emission characterization data for chemical mass balance application are unlike those intended to simply measure particulate mass emissions. For application in CMB analysis, EPA method 5

Table 13. Chemical Mass Balance Input Source Composition Consideration*

<u>Source Class</u>	<u>Literature Review Considerations</u>
Motor Vehicles	° Leaded/unleaded/diesel vehicle mix ° Br/Pb ratio (fresh or aged aerosol) ° Smoke suppressant use in diesel fuels ° Transportation source mix near the receptor
Soils	° Study area soil chemical "enrichment" by local emission deposition ° Local soil composition consistency with literature values ° Importance of limestone to local soils
Residual Oil Combustion	° Similarity in the fuel elemental composition ° Use of fuel additives ° Combustion system similarity
Coal Combustion	° Similarity in chemical composition of input fuel ° Similarity in combustion process and control system type and efficiency
Vegetative Burning	° Similarity in type of fuel burned ° Point(s) within the combustion cycle where sampling occurred
Metals Industry	° Specific process sampled, control equipment used and chemical composition of the alloy ° Point(s) within the process cycle sampled

* In all cases, the particle size of the source emissions reported in the literature must be known and considered in relation to the size cut used in the ambient monitoring program.

emissions. Since emissions from some sources are especially "rich" in easily measured chemical species, it is important that they be accurately characterized.

4.2.2 Source Testing Protocol

Source testing protocols for emission characterization studies vary widely among receptor model users, some relying on multistage in-stack cascade impactors while others prefer aircraft plume studies. Perhaps the most feasible, cost-effective methods, however, are those designed to capture condensable aerosols with the use of stack gas dilution sampling trains. Systems designed with dichotomous impactors or cyclones have provided fine and coarse mode samples suitable for trace element, ion and carbon analysis have been used in several source apportionment studies. Unfortunately, none of the methods have been well documented in the open literature or are commercially available. Those interested in obtaining "state-of-the-art" information on source test train design for CMB studies are encouraged to contact EPA's Technical Support Staff, Industrial and Environmental Research Laboratory (IERL), Research Triangle Park, North Carolina.

Regardless of the protocol used, selection of the proper filter media is of utmost importance. The ideal filter used for chemical analysis should meet the following criteria:

1. Mechanical stability: The filter cannot deform or break under routine operating procedures. Ease of handling is also an advantage.
2. Chemical stability: The filter must be stable enough to withstand required variations of temperature and treatment without decomposing or interacting with the aerosol deposit.

source testing protocol is not necessary, velocity traverses are not required, nor are measurements of stack gas CO₂ concentrations needed. The intent is to capture a representative portion of the particulate matter on a filter substate, in a manner suitable for chemical analysis of trace elements, ions and/or carbons. Only those characteristics of the source, as perceived at the receptor, are important. Recent studies have used stack gas dilution equipment designed to capture condensible organics and other volatile species.³⁴ Regardless of the protocol used, the source characterization program must provide data which meet the following criteria:

1. Sources selected for testing must be representative of other, similar sources found in the airshed.

2. Samples must be taken during steps in the process cycle which are representative of the source emission chemistry and are important emission events.

3. The sampling program must be designed to insure that most major emission sources or source classes are sampled.

4. A sufficient number of samples must be collected during each series of tests to determine the variability in the chemical composition of the particulate.

5. The source testing protocol must be consistent with analytical requirements.

6. Information on the chemical composition of the process input materials (or fuels), process conditions and control equipment status must be collected at the time of sampling to insure proper program documentation.

Each of the six criteria noted above are important aspects of a successful program.

4.2.1 Selection of Sources for Testing

The number and type of sources to be included in the source characterization program should account for as much of the known emission inventory as possible. All major sources of each measured species and any suspected large point or area source which has not been previously inventoried should also be included. After a source class has been targeted for testing, the specific source(s) included within that category should be selected, based upon the individual source's total emissions, the representativeness of the source in relation to its source class, and the likely impact of the source on the air quality at critical receptors. The latter requirement should be based on dispersion model results or other airshed studies of source impacts. To insure that all major sources of important chemical species are included in the testing program, source composition data reported in the literature can be used in concert with existing particulate emission inventory data to compile a "chemical emission inventory" which, in turn, is used in assuring that "element-rich" sources are characterized. If, for example, emissions from steel manufacturing are estimated at 38 tons/year and Cr is estimated to be 2.1% of the mass (Table 5), then about 0.8 tons/year of Cr is emitted by steel processing sources. Expressed as a percentage of the total estimate Cr emissions found in an airshed, the analyst can quickly evaluate chromium's uniqueness as a "tracer" for steel mill

3. High particle collection efficiency: Particles in the size range of interest must be removed by the filter from the air passing through it.

4. Low flow resistance: A lower resistance to airflow through the filter increases the volume of air that can be sampled in a given time with a given pump.

5. Good retention without clogging: An acceptable quantity of deposit must adhere to the filter without clogging filter pores to the extent that the flow rate declines. Note that conditions 3, 4 and 5 require some tradeoff among them.

6. Low and consistent blank values and artifacts: The properties being sought of the aerosol should not be interfered with by the properties of the filter. To the extent that they are, the filter influences should be constant so that they may be subtracted.

7. Cost and availability: The manufacturer must be a dependable supplier of a constant quality product and his cost must be within the limits imposed by the financing of the study.

For routine XRF analysis, two additional conditions are imposed.

8. Homogeneous surface deposit: The aerosol must form a homogeneous deposit on the surface of the filter. Uneven distribution of aerosol throughout filter would require x-ray absorption corrections which are difficult to quantify.

9. Low area mass density: The scattered primary radiation intensity is directly proportional to the mass per unit area of the filter material. A low mass per unit area assures low background in the x-ray spectra and greater sensitivity for the elements being quantified.

Although each commercially available filter meets these criteria to varying degrees, no one filter satisfies all of them. In practice, the filter substate used is selected by evaluating each filter's specification in relation to program priorities. For source testing, the temperature and humidity extremes anticipated, the source loading characteristics and the filter handling requirements are all key considerations.

Source samples should be collected using sampling systems which duplicate the size cuts obtained in the ambient sampling program. To ensure accurate fine/coarse mass ratios, isokinetic sampling techniques (i.e., sampling at the same velocity in the probe as in the stack gas) should be used.

New approaches for characterization of particles from sources are needed to overcome the deficiencies of stack sampling noted above. For use with receptor models, it would be desirable to collect particles far enough out of the stack for gas phase species to have condensed, for coagulation of fine particles in the stack emissions to have occurred and for any very large particles to have settled out of the plume. Possible new methods of sample collection could include the use of in-plume sampling using tethered balloons and aircraft. As presently done, source sampling with balloons does not permit sufficient payloads to assure capture of large enough samples or the use of size-segregating samplers. Further developments are also needed in aircraft sampling to increase sampling

flow rates while maintaining isokinetic conditions and avoiding perturbations of samples by the aircraft itself. A high volume impactor or dichotomous sampler for use in airplanes that can be operated isokinetically is badly needed.

Some in-stack procedures are being developed which will yield results that are compatible with the requirements of receptor models. These include size segregating in-stack cascade impactor, dilution source sampling systems^{34,35} and dichotomous samplers adapted to source sampling.²³

5.0 AMBIENT AEROSOL CHARACTERIZATION REQUIREMENTS

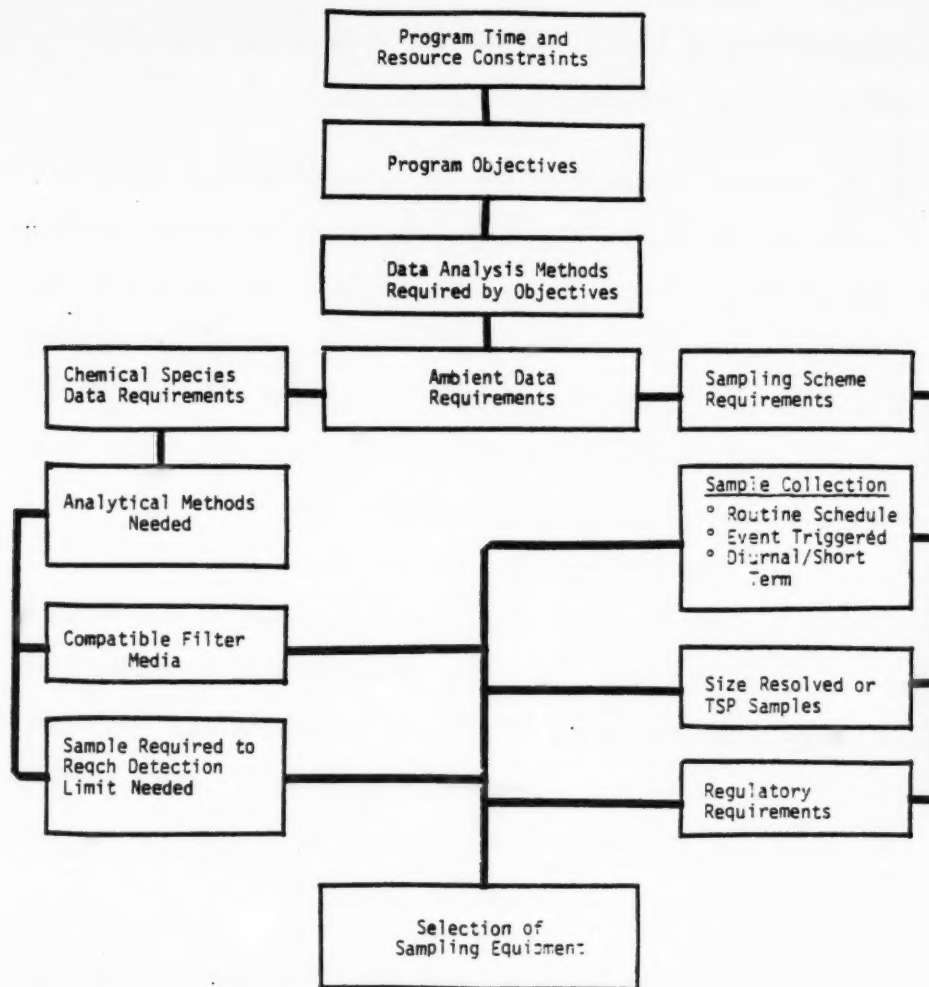
The scope of the ambient aerosol characterization requirements includes the program air sampling design (selection of sampling systems and schedules, filter media, logistics, etc.), the analytical program (determination of chemical species to be measured, analytical methods and laboratory quality assurance), as well as the verification and management of the data. Each of these considerations must be incorporated into the overall program design.

Much can be done to maximize the likelihood of successfully utilizing the CMB model. Typical "tricks" used to maximize source impact signatures detected by CMB include (a) the collection of larger particulate mass loading by either extended sampling time or using high flow rate samplers, (b) maximizing analytical precision and accuracy, (c) minimizing detection limits, (d) maximizing the likelihood of the source impact by carefully selecting sampling times and locations, and (e) collection of samples within the size range most likely to be impacted by the source under investigation. During the data analysis phase, care must also be taken not to "smear" the ambient chemical species data by averaging data sets over long time periods.

5.1 Sampling Program Design

Perhaps the best approach to designing a sampling program is to first identify the amount of time available to conduct the program and the resource constraints. Next, a review of program objectives and identification of the data analysis techniques to be used is drafted and reviewed. If the requirements of the data analysis techniques are understood and analytical approaches are identified that can provide the needed information, a sampling program can then be developed that meets all of the analytical system constraints. Figure 6 illustrates the

Figure 6
Sampling Equipment Selection
Block Diagram



planning process required to identify the sampling hardware requirements. Use of sampling equipment because it is already in the current inventory is often not the best solution, as the analytical program requirements may be seriously compromised. Regardless of the devices selected, the particle size cuts (if any) of the sampler and their dependence with respect to windspeed and direction should be known if comparability of results between the study, other programs and future regulatory action is to be achieved.

For sampling in which knowledge of the variation of aerosol concentrations with time is required, the sampler should be able to switch filters sequentially without operator attention. Table 14 lists commercially available sampling systems typically used in source apportionment studies. Camp³⁶ has reported on an intercomparison of these, and other, samplers. Because of the re-entrainment and particle bounce problems associated with cascade impactors, which cause large particles to penetrate to the small particle stages, dichotomous (virtual) impactors and cyclone preseparator systems are the most commonly used size separating devices in current aerosol characterization studies. In most studies, particularly those in which regulatory issues are addressed, a 24-hour high volume sample should accompany samples taken with other devices. The relationship of the aerosol study samples to the historical total suspended particulate matter data base can be evaluated through a comparative analysis of the two data sets.

Meteorological information which has been useful to receptor model studies includes temperature, relative humidity, mixing height, windspeed, and wind direction. The wind direction is particularly important for the verification of certain source contribution predictions obtained with receptor models (see Chapter 6.0).

Table 14. Aerosol Source Apportionment - Sampling Equipment

Manufacturer (model)	Sampling Rate (lpm)	Upper Cut Point	50% MMD Diameter	Typical Sampling Period	Approximate Cost	Filter Size	Notes
Anderson (3000)	16.7 lpm*	15 μ m	2.5 μ m	24 hr.	\$4000	37mm	Dichotomous sampler, Virtual impactor
Beckman (ENVIRO-SAMP)	16.7 lpm*	15 μ m	2.5 μ m	24 hr.	\$6000	37mm	Automated filter changing - Programmable for short-term sampling. Dichotomous sampler, virtual impactor.
ERAT** (fine fraction)	70 lpm	2.5 μ m	-	24 hr.		47mm	Samples only a single size fraction, cut point dependent on cyclone preseparator used.
ERAT (total or inhalable fraction)	70 lpm	~30 μ m	-	24 hr.		47mm	Automatic filter sequencing for short term sampling
Sierra (244)	16.7 lpm*	15 μ m	2.5 μ m	24 hr.	\$4000	37mm	Dichotomous sampler, Virtual impactor
Sierra (245)	16.7 lpm*	15 μ m	2.5 μ m	24 hr.	\$6000	37mm	Automatic filter changing allows short-term (4, 8 or 12 hr.) sampling. Dichotomous sampler. Virtual impactor.

*15.0 lpm - fine, 1.7 lpm - coarse flow rate

**Environmental Research & Technology

NOTE: At the time of this writing, 10 μ m retrofit inlets are being developed for these instruments.

The frequency and duration of aerosol measurements are also important factors, since source contributions are often of a short-term nature. To measure the variability in the aerosol composition requires sampling times of the same order as that variation. Twenty-four hour sampling is often considered to be the longest acceptable sampling time and shorter term sampling is often desirable. Measurements needed to extrapolate the data to annual average conditions may also be required. Depending on the program objectives, it may also be important to obtain information during episodes and under relatively clean conditions. Thus, more samples than needed should be collected with a subset chosen for detailed chemical analysis.

Instrument siting should be consistent with EPA criteria as specified in 40 CFR 58 Appendix E (May 10, 1979 Federal Register), unless the program objective is to study impacts of a single specific source. In many cases, existing National Air Monitoring Sites (NAMS) and/or State and Local Air Monitoring Sites (SLAMS) are used for reasons of access, availability of historical data and the availability of supportive data from other samplers. These sites are also used because they often represent the location at which data are taken to determine NAAQS attainment/maintenance status. It is at these sites that interest in source contributions and aerosol composition is often focused.

Although much information can be gained from data located at a single site in an urban center, multiple samplers located within nonattainment "hot spots" or areas of projected maximum plume impact are often needed to insure sufficient spatial coverage. "Background" data captured upwind of the urban area (or source of interest) is extremely helpful in isolating "local" from "background" aerosols. In either case, extreme care must be taken to insure representative instrument siting.

5.2 Analytical Program Design

The chemical components to be quantified in each sample and the analytical methods to be used should be specified before the first sample is taken. The experimental design must also be reviewed to assure that the field samples will be amenable to the chosen analysis techniques. This requires a comparison of specie concentrations likely to be found in the ambient samples to the lower quantifiable limits of the analytical methods. The sampling design or analytical method must be modified if the majority of the expected ambient specie concentrations are less than the detection limits. Filter media must be selected which will not bias the aerosol measurement because of variable blank concentrations or artifact formation. If x-ray fluorescence is to be used, the aerosol must be deposited on the surface rather than inside of the filter to prevent absorption of x-rays by the filter material. Simultaneous sampling on more than one substrate may be required.

Each analytical method must be judged in terms of four necessary and three desirable criteria. These apply not only to the analytical method, but to the laboratory performing the method, as well.

The necessary criteria are:

1. The analytical method must have been developed and tested specifically for the analysis of suspended particulate matter.
2. Lower quantifiable concentrations of the method must be less than the concentrations expected from the ambient samples taken.

3. The method must be relatively free of biases for all components quantified.

4. The values achieved by the method must be reproducible within defined and reasonable confidence intervals.

If an analytical method is successful for certain types of environmental samples, it is often convenient to assume that it is appropriate for all samples. Hard and bitter experience shows this not to be the case for suspended particulate matter. Before a procedure can be accepted, one must have identified and corrected likely interferences, defined compatible aerosol collection substrates and sampling requirements, and verified the procedure's ability to meet criteria 2 through 4.

The amount of suspended particulate matter available for analysis depends on the ambient concentration, the flowrate of air through the substrate, the sampling duration, and the fraction of the sample presented for analysis. The expected amounts available for analysis should ideally be a factor of ten or more above the lower quantifiable concentrations of the analytical method.

Measurement accuracy can only be established through interlaboratory/inter-method comparisons and the analysis of standard reference materials. Intermethod comparisons are better for evaluating accuracy since interlaboratory analyses using the same method will exhibit the same types of biases. Urban Particulate Matter Standard Reference Material 1648 provides a means for initial and routine verification of accuracy. The concentrations of additional chemical components in this standard need to be quantified and their constancy with time assessed. NBS 1648 was collected in St. Louis and is representative of the eastern city

aerosol matrix. Other aerosol standards from a variety of locations would be helpful for the evaluation of analytical bias.

Replicate analyses of the same sample should return results with a standard deviation of $\pm 10\%$ or less at concentrations greater than ten times the lower quantifiable limit for most species. The data from replicate analysis should be used to define the precision of each value measured.

Three additional desirable criteria for analytical methods are:

1. The method should measure a number of components in a single analysis.
2. The analysis should be nondestructive.
3. The analysis should be cost-effective.

Many analysis techniques are capable of measuring more than one chemical component of interest with adequate precision, accuracy and sensitivity. Not only do these methods save the cost of many individual analyses, they minimize the amount of sample required.

A nondestructive method is preferred since the sample can be made available for other analyses to verify the nondestructive results or to complement them with the measurement of additional chemical components.

Given the choice of analytical methods meeting the necessary and desirable criteria, the least expensive analysis per sample should be chosen. This choice may vary with the number of samples to be processed. Table 15 lists some common analysis techniques and the elements most commonly measured by them.

Table 15. Techniques for Elemental Analysis*

Element	NA	PA	XRF	XRFS	XPA	PS	AAS	ES
Li						X	X	
Be						X	X	X
B						X		
C						X		
N						X		
O						X		
F					X	X		
Na	X			X	X	X	X	
Mg	X				X	X	X	
Al	X		X	X	X	X	X	X
Si		X	X		X	X	X	
P						X		
S	X	X	X			X		X
Cl	X	X	X		X	X		
K	X	X	X				X	
Ca	X	X	X	X	X		X	
Sc	X							
Ti	X	X	X	X	X		X	
V	X	X	X	X	X		X	X
Cr	X	X	X	X	X		X	X
Mn	X	X	X	X			X	X
Fe	X	X	X	X	X		X	X
Co	X		X	X			X	
Ni	X	X	X	X	X		X	X
Cu	X	X	X	X	X		X	X
Zn	X	X	X	X	X		X	X
Ga	X		X		X			
Ge	X			X				
As	X		X	X	X			
Se	X		X		X			
Br	X	X	X	X	X			
Rb	X		X		X		X	
Sr	X		X	X	X		X	
Y					X			
Zr			X	X	X			
Mo	X			X				
Rh					X			
Pd			X					
Ag	X				X			
Cd	X		X		X		X	X
In	X				X			
Sn	X		X	X			X	X
Sb	X		X		X			
I	X				X			
Cs	X				X		X	
Ba	X		X		X		X	X

Table 15. Techniques for Elemental Analysis* (continued)

Element	NA	PA	XRF	XRFS	XPA	PS	AAS	ES
La	x							
Ce	x			x	x			
Nd	x							
Sm	x							
Eu	x							
Gd	x							
Tb	x							
Dy	x							
Er					x			
Tm				x				
Yb	x				x			
Lu	x							
Hf	x				x			
Ta	x							
W	x			x	x			
Os					x			
Ir					x			
Pt					x			
Au	x				x			
Hg	x		x	x	x		x	
Pb		x	x	x	x		x	
Bi							x	x
Rn								
Th	x							
U	x		x					

* Abbreviations:

- NA = Neutron activation
- PA = Proton activation (charged-particle induced XRF)
- XRF = X-ray fluorescence
- XRFS = X-ray photon activation
- PS = Proton scattering
- AAS = Atomic absorption spectroscopy
- ES = Emission spectroscopy

SOURCE: Reference 5

5.2.1 Elemental Analysis Techniques

The variety of analytical methods available for elemental analysis of aerosol samples has been reviewed by Katz.³⁷ Several of these methods meet the three criteria mentioned earlier - multicomponent analysis by a nondestructive technique which is highly cost effective. With the exception of perhaps hydrogen and oxygen, most elements of known or suspected utility to aerosol source-receptor studies can be measured by a combination of elemental analysis techniques. Unfortunately, not all important elements can be determined by a single technique.

X-ray fluorescence (XRF), using photon or proton excitation, has developed into a reliable, cost effective elemental analysis technique that has been widely applied in aerosol studies.³⁸ More aerosol samples, probably numbering in the hundreds of thousands, have been analyzed for elemental components by this method than by any other. The technique requires aerosol samples uniformly deposited on a thin, flat organic substrate (Teflon, Nucleopore, polycarbonate or cellulose acetate membrane filters) that are also simple to handle, easy to weigh and commonly used in ambient dichotomous samplers. In typical urban samples, 10 to 20 elements can be routinely measured by XRF. Problems may be encountered in the measurement of lighter elements (Na, Mg, Al) in coarse mode particles, requiring data corrections. Hi-vol samples collected on glass fiber filters are inappropriate for XRF analysis because of the penetration of the particles in the filter matte. Interlaboratory and intermethod comparisons have verified the accuracy and precision of XRF.³⁶

Instrumental neutron activation analysis (INAA) is another multi-element, nondestructive technique widely used in aerosol studies.³⁹ INAA is commonly used to supplement XRF analysis by providing accurate measurements of

the lighter elements in common with XRF for quality control purposes, and by providing a measure of rare earth elements not detected by other methods. Although INAA equals or surpasses XRF methods in sensitivity for many elements, it is more labor intensive than XRF and is therefore more costly. Particles can be measured either in bulk form or, as a thin deposit, dichotomous sampler filters. Samples collected on glass fiber substrates have been analyzed by INAA,⁴⁰ but due to the high and variable elemental blank content of the filters, their use is not recommended.

Atomic Absorption Spectroscopy (AAS), Atomic Emission Spectroscopy (AES) and Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICP/AES) are all destructive techniques which require sample dissolution. AAS and AES are single element methods while ICP/AES provides multielement detection. Since the samples must be brought into solution, the aerosol can be collected in bulk or on a filter substrate. These methods are less widely used than XRF and INAA because of the destructive nature of the techniques, their lower cost effectiveness for most multiple sample analysis, and the highly variable extraction efficiencies for many elements.

5.2.2 Carbon Analysis

Unfortunately, the carbon content of aerosol samples cannot be reliably measured using XRF, INAA or AAS techniques. Analysis of the aerosol's carbon content is important if the analyst wishes to chemically apportion all of the aerosol mass. Since currently available carbon analysis techniques require that the aerosol be captured on a binderless glass or quartz fiber substrate, collocated samplers are often required to capture aerosol samples appropriate for both elemental and carbon analysis.

techniques, can provide significant information about the mineral content (and additional compounds) in aerosol samples. Microscopy is also a very useful analytical tool.

Additional techniques such as ESCA, Auger Electron spectroscopy, Raman spectroscopy, and IR absorption can provide different types of chemical information which may find great utility in aerosol composition studies. Active development of these techniques is underway.⁴¹

5.2.6 Sample Analysis Priorities

X-ray fluorescence is generally accepted as the most reliable, available and cost-effective nondestructive method for elemental analysis of aerosol samples. Instrumental Neutron Activation Analysis is a powerful second choice which offers many advantages over XRF but is more costly. The combination of the two methods offers the most complete and reliable data sets. Other desirable analyses include those for inorganic and organic carbon, as well as ion analyses. Although the cost effectiveness of the analytical method will vary among airsheds because of differences in chemical source "tracers," one suggested rating is as follows:

1. Mass
2. Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Pb by XRF
3. Carbon, sulfate, nitrate, ammonia
4. Elemental and organic carbon; Na, Mg, Al, Ti, V, Mn, Br by INAA
5. I, Sc, Cr, Fe, Co, As, Se, Cd, Sb, La, Ce, Th by INAA

Most analytical techniques are based on sample combustion in oxygen, followed by CO_2 measurement, or conversion of the CO_2 to CH_4 , followed by flame ionization detection. Other atmospheres and combustion temperatures can provide a measure of the elemental and organic carbon content (see Section 3.2.1) that is extremely helpful in apportioning carbonaceous sources using CMB. Other methods based on nuclear techniques, solvent extraction and Laser light absorption techniques have also been used.⁴¹

An important development in the measurement and classification of carbon for source apportionment is the quantification of ^{14}C in particulate matter by low level counting techniques.⁴ These techniques provide an estimate of the portion of aerosol carbon contributed by fossil fuel combustion sources (oil, gasoline, diesels) as distinguished from "contemporary" carbon sources such as wood burning. Used in conjunction with the organic/elemental carbon technique discussed above, the ^{14}C technique may be able to distinguish that portion of the fine particle organic carbon fraction associated with fossil and "contemporary" sources. By applying CMB analysis, the portion of organic carbon not assigned to other sources (usually considered to be secondary carbon) can be further apportioned to determine the portion of the secondary carbon from vegetative emissions versus those from evaporative losses associated with fuel storage.

5.2.3 Ion Analysis Methods

The ionic species (e.g., NH_4^+ , Cl^- , SO_4^{2-} , NO_3^- , H^+) are important components of the fine particle mass. They can also serve as an important "fitting" element in CMB analysis since some source emissions (e.g., Kraft Recovery furnace emissions) are particularly rich in ions. A wide variety of ion analysis methods exist which have adequate sensitivity for aerosol analysis. All

of the methods are destructive, requiring dissolution of the sample. This is commonly done following elemental analysis by nondestructive techniques (Section 5.2.1). For CMB studies, ion chromatography is often used because of ability to measure several ions (or cations) simultaneously.⁴² Automated colorimetry methods have also been used extensively. Practically all collection substrates are compatible with these two techniques. Artifact formation, particle to particle interactions, gas-particle interaction and contamination, and sample storage are important considerations in the sampling process.

5.2.4 Organic Compounds

The organic compounds (e.g., PAH, acids, heavy alkanes, etc.) are of great potential for use in aerosol source receptor studies. Chromatography (liquid and gas), mass spectrometry and other techniques have been used to study organic compounds in the atmosphere.⁴¹ Information about source emissions of organic compounds and their stability in the atmosphere is required if usable tracers are to be identified. Unfortunately, this information is extremely limited in scope. Nevertheless, organic measurement techniques for use in source receptor studies is an area of great current interest and activity.⁴³ Specific procedures may now be useful for certain types of studies. This whole area of analytical atmospheric chemistry should be closely watched as rapid improvements and developments are expected.

5.2.5 Molecular Composition

Techniques for determining the molecular composition of aerosols are currently becoming available. X-ray diffraction (XRD) can provide qualitative and quantitative information about crystalline species, inorganics and organics, contained in aerosol samples.⁴⁴ XRD, when used in conjunction with microscopic

5.3 Data Stratification

Important savings in analytical costs can often be achieved through the use of sample or data stratification techniques. Three approaches have been used in recent CMB studies:

(A) Stratification of Sample Analysis Data

Analytical results obtained from a number of samples, collected during periods of similar weather, source impact scenarios, air quality, time of day, or other conditions, can be averaged together to provide a single data set which is then used to perform a single CMB calculation. Cost savings in data analysis time tend to be offset by the loss in short term source apportionment results (e.g., daily trends in soil dust impacts) which can provide important clues as to the origin of particles. Although the averaging process tends to minimize analytical errors from individual filters, the ability of the CMB model to resolve minor source impacts is usually impaired by the "smearing" of the aerosol fingerprints.

(B) Stratification of CMB Calculations

Rather than averaging analytical results across a large number of samples, CMB calculations can be performed on data sets developed from a single, 24-hour sample. Source impact estimates can then be stratified by weather regime, source activity, visibility, or other parameter. While this approach offers little cost saving advantage, the averaging process tends to provide source impact estimates that are less sensitive to analytical error than those developed from single sample data sets.

(C) Sample Composite Analysis

Groups of samples collected during periods of similar selected conditions may be grouped together within a single analysis to provide one set of analytical data. The advantage to this approach is that it greatly reduces analytical costs and improves analytical sensitivity. The process may, however, distort the ambient particle species patterns and complicate the CMB model's ability to resolve minor source impacts.

The most effective source resolution data sets (and the most costly) are those which include individual filter analysis and CMB calculation, since they provide a more extensive volume of data. Sample composite analysis techniques are extremely cost effective where chemical composition data is used as a direct indicator of source impact (e.g., wood smoke impact analysis based on carbon-14 measurements).

5.4 Quality Assurance

The development of sound quality assurance procedures for the field and analytical programs are extremely important to assuring the credibility of an aerosol study, especially when the results are likely to form the foundation of future control strategies. Key elements of the program should include:

- ◊ Standard operating procedures for sampler operation, logistics, analytical programs and data handling;
- ◊ Adequate frequency of instrument/sampler calibration and audits;
- ◊ Interlaboratory and intermethod comparisons on at least 10% of the samples;

- ° An adequate level of filter blank analysis;

- ° The determinations of sampling and analysis error are required as are error bands in each completed analysis if the error propagation scheme incorporated in the CMB effective variance solution is to be used;

- ° Data verification and preliminary screening before the final stages of data interpretation are reached;

- ° Occasional reviews of field and laboratory operation by project management and data analysts;

- ° Clear documentation of analytical procedures.

Care must be taken to insure that all field and laboratory procedures are insuring good quality data before these programs become fully operational. Hard experience has shown that failure to assure that high quality samples and lab analysis have been achieved is to invite major failures in the entire program.

5.5 Data Management

The final important ingredient of experimental design is data management, which is normally carried out by computer. The data must be organized and merged into uniform formats accessible by the receptor models. Provisions for the entry and processing of quality assurance data will greatly reduce the efforts required for this often neglected study component. All data from initial analyses must be retained until the sorting of relevant and irrelevant information can be achieved. Economical accessibility, security and definition of uncertainty should be keynotes of data management systems for this work. Organization techniques for easily extracting subsets of data from large data bases are often

needed to maximize economic data handling and computation.

Though the sampling, analytical and data management tasks are presented here as separate entities, each requires an awareness of its interaction with the others. No two program designs will be alike, but studies with similar goals will usually be of similar design.

6.0 EVALUATION OF CMB RESULTS

Although this chapter focuses on verification of CMB model results, an equal degree of care should be taken in evaluating the quality of the CMB input data. As a first step, evaluations of laboratory analytical precision within and between analytical methods, correlation analysis of fine particulate mass - scattering coefficient (B_{scat}) data and comparisons of data collected at different sampling sites may be helpful. Evaluations of the quality of the input data and correction of deficiencies are most important to the successful use of the CMB method within the context of airshed studies.

The process of evaluating CMB model results is of central importance to the credibility of study findings. Four criteria may be used to assess the validity of the apportionment analysis, each of which is discussed in further detail in the following sections:

- ° Model results must be internally consistent (e.g., predicted/observed specie and mass agreement, correlations among elements from a common source, reproducibility of results).
- ° Estimated source impacts should agree with source activities, transport and dispersion conditions within the airshed.
- ° Source apportionment results should be consistent with impact estimates derived by other techniques such as dispersion modeling, multivariate statistical methods, microscopy, or other receptor model approaches.
- ° Unexpected results should be investigated and explained.

Unfortunately, there are no clear standard or "right" answers against which CMB-estimated source contributions can be compared to determine their validity. Results can, however, be evaluated in terms of results from other methods, the relative merits of each approach identified and judgments made relative to the credibility of the CMB results.

6.1 Internal Verification Techniques

In the absence of "hard" standards for comparison, the credibility of CMB results can best be judged by applying as many self-consistency tests as possible. Gordon⁴⁵ has suggested three criteria to evaluate the quality of CMB fits:

- A) The concentrations of all species and each size fraction's mass should be predicted accurately.
- B) The predicted size distributions of the sources determined by CMB should be consistent with the size distributions measured at the receptor.
- C) Concentrations of chemical species should be highly correlated with other species thought to come from the same source.

Criterion A is best evaluated by examining the average CMB-predicted/observed species and mass data derived from a large number of individual samples. Predicted/observed (pred/obser) specie ratios within the range of 0.5 to 2.0 are generally considered acceptable. Ratios that fall outside of this range may indicate an error in accounting for an important source (as is common in coarse-mode Ca, for example), errors in the source composition, element volatility or the presence of a previously unaccounted for source (e.g., sampler vacuum-pump motor particulate indicated by a low Cu predicted/observed ratio).

Mass pred/obser ratios within a range of 0.8-1.1 are difficult to achieve unless nearly all of the aerosol mass has been accounted for chemically. In those cases where only partial elemental and ion data are available, such as from the EPA inhalable particulate network, mass ratios much less than 0.8 are to be expected because of the absence of water, oxygen, hydrogen, and carbon components in the analysis. Supplemental analysis for these components would be necessary in airsheds where important constituents of the aerosol have not been included in the analytical protocol.

Criterion B requires that the percentage of each source's impact (at the receptor) estimated for the fine mode ($\leq 2.5\mu\text{m}$) should approximate the percentage of emissions (at the source) found in the same size fraction. If, for example, 90% of the emissions measured in a boiler's stack are found in the fine mode, one would expect to find most of the boiler's impact measured at the receptor in the fine mode. Gordon's⁴⁵ analysis of these results from the Portland Aerosol Characterization Study, summarized in Table 16, shows that for most sources the agreement between the fraction of mass in the source emissions and that estimated by CMB is reasonable. Source impact estimates for vegetative burning emissions, for example, often do not agree, due to the large uncertainty in the source's composition and the chemical similarity between coarse-mode vegetative burning particles and plant tissue. Disagreement between estimates for minor source components are to be expected because of relatively large analytical and fitting errors near the limit of the method.

Table 16

Portland Aerosol Characterization Study:
Percent of Fine Mass in Source Emissions
Versus Impact at the Receptor

<u>Source Class</u>	<u>Receptor (CMB Estimate*)</u>	<u>Source Emissions</u>
Marine	44	50
Urban Dust	4	10
Motor Vehicle	68	80
Residual Oil	68	90
Vegetative Burning	49	99
Aluminum Processing**	20	56
Sulfate Recovery Furnace **	95	90
Hog Fuel Boiler**	100	73
Steel Manufacturing	38	92
Ferromanganese Production**	61	92

* Downtown Portland, annual average

** Minor components ($<0.2\mu\text{g}/\text{m}^3$)

Because of preferential deposition of particles emitted in the coarse mode ($>2.5\mu\text{m}$), application of this criterion to the coarse mass provides less certain results. As an upper limit, one would expect to find a greater percentage of a major coarse particle source (e.g., urban dust) in the source emission than in the receptor samples.

Criterion C suggests that binary correlations between species measured at each sampling site be examined to see if the results are consistent with CMB findings. By stratifying data sets into CMB-estimated source impact groups, the investigator can examine "impact" versus "no impact" correlation sets for significant elements common to the source class being examined. For example, one would expect a higher correlation between fine particle Fe and Mn during impact from a steel mill (as measured by CMB) than during a period of no impact.

Reproducibility in model results is also an important internal test of the CMB model. Tests of source strength variability by Watson²³ using simulated data sets showed that the number of species included in the fit, the degree of uncertainty in the ambient and source composition input data and the mathematical solution to the set of simultaneous equations (tracer, ordinary weighted least square or effective variance least square solution) were all important considerations to the ability of the model to accurately predict source strengths. To test the sensitivity of the CMB model to error in the input data, Watson assumed a random 20% uncertainty in each chemical specie. Ten data sets were generated and independent fits were developed for a synthetic set of four sources: marine air, urban dust, auto exhaust, and residual oil. The results listed in Table 17 were obtained. In general, Watson found that it is advantageous to use as many fitting species as possible and that the effective variance solution seems superior in most cases.

Table 18 illustrates the variability in urban dust source strength under the test conditions, given a "true" source impact of 35 $\mu\text{g}/\text{m}^3$. For comparison, the source strengths estimated using Si and Al as tracers are also presented. The much wider variability in tracer-derived source strength attests to the value of using a number of species in the fitting process.

6.2 Source Activity and Transport Methods

An analysis of anticipated source strengths, preferably conducted independently from those involved in the CMB analysis, can provide important clues regarding the validity of the receptor model analysis. This requires, however, the prior assumption that source activity or transport analysis represents the "truth" against which the CMB results can be judged. Such an assumption may be very misleading.

Table 17. Reproducibility of CMB Model Results
(Synthetic Data Set with 20% Uncertainties*)

Source	True Source Contribution $\mu\text{g}/\text{m}^3$	Average Results $\pm 1\sigma$	
		N = 8**	N = 23*
Marine air	20	16.6 $\pm$ 3.8	15.9 $\pm$ 2.2
Urban dust	35	29.2 $\pm$ 6.1	32.9 $\pm$ 4.9
Auto exhaust	30	29.6 $\pm$ 8.0	27.0 $\pm$ 3.8
Residual oil	15	13.9 $\pm$ 2.0	14.5 $\pm$ 1.6
Total	100	89 $\pm$ 11	90 $\pm$ 7

* Species included in the fit were NO_3^- , SO_4^{2-} , F^- , Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb, organic and elemental carbon

** Na, Al, Si, Cl, V, Ni, Br, and Pb included in the fit

Table 18. Variations in Urban Dust Source Strength Within Ten Independent CMB Solutions*

Solution	Effective variance 23 fitting elements	Si tracer Solution	Al tracer Solution
1	34	20	40
2	33	26	43
3	36	36	46
4	32	20	31
5	41	45	37
6	25	20	43
7	28	35	36
8	28	34	23
9	36	31	37
10	33	36	33
Average	32.6 $\pm$ 4.7	30.3 $\pm$ 9	36.9 $\pm$ 6.7

* Chemical specie concentrations perturbed at the 20% uncertainty level

The ability to prepare graphical comparisons of temporal changes in source activity versus CMB-derived source strength, reflects one of the strong points in the CMB approach compared to multivariate techniques because of the latter's requirement for large sets of data. Table 19 suggests several comparisons that may prove useful in evaluating CMB results.

Table 19
Comparison of CMB Results with
Temporal Changes in Source Activity

<u>CMB-Source Class</u>	<u>Source Activity Indicator</u>
Motor vehicle	Diurnal, weekday-weekend traffic volume changes
Marine air	Marine air frontal passages
Vegetative Burning	Smoke intrusion reports by forestry agencies, heating degree days
Industrial Processes	Labor strikes, maintenance shutdowns, changes in control system efficiency

Spatial variations in source class emission density can also be used to evaluate CMB source strength estimates. Concurrent CMB-derived source strength estimates for each source class obtained from a number of sampling sites can be used to develop isopleth maps which can be superimposed on emission density maps. Less resource intensive evaluations based on microinventory results can also be used.

Atmospheric transport information can provide strong support for attempts to resolve impacts from specific sources within a general CMB source class. If, for example, an airshed was impacted by two steel mills having chemically similar emissions, the individual impacts can be identified by (a) sampling during periods of persistent wind direction at a point downwind of the source of interest,

yet upwind of the second mill, (b) CMB results can be stratified for wind direction and stability cases likely to favor impact from a specific source, or (c) source strength data from two or more sources can be used, in association with wind direction data to identify sources by "triangulation."

The triangulation technique requires that the program design include four key elements:

- (1) Analysis of historical hourly wind direction data (θ) to determine the frequency and standard deviation ($\sigma\theta$) of winds within 22.5° sectors during the period within which ambient sampling is to occur.

- (2) Placement of sampling sites downwind of major sources using information developed during step 1.

- (3) Collection of very accurate, hourly wind direction data at one or more sampling site during the period of the field program.

- (4) Collection of 12, 8 or 6 hour, size resolved, ambient aerosol samples timed to capture samples during likely periods of maximum source impact.

Gordon⁴⁶ has used triangulation methods to investigate periods of high wind persistence (hourly wind direction standard deviations of $<20^\circ$) during the occurrence of unusually high concentrations of "tracer" elements in St. Louis aerosol. Wind trajectory maps for each sampling site, for each element have been drawn which intersect at a dominant source of the elements. The source is then identified by emission inventory maps. Although the method has potential as an independent means of qualitatively identifying source impacts against which CMB estimates can be correlated, the method does not seem useful for area source

emissions (e.g., soil dust, etc.) or sources emitting ubiquitous chemical species. Current research suggests that "triangulation" techniques may also be useful to deduce the composition of source emission as they exist at the receptor, rather than in the stack.

6.3 Comparisons to Other Techniques

Many of the source apportionment methods shown in Figure 1 (page 3) can be used to evaluate CMB results. Coarse mode soil dust impacts obtained by CMB analysis can, for example, be compared to x-ray diffraction or optical microscopy results if care is taken to protect and preserve a portion of the sample. Radio-carbon, enrichment factor and CMB results for vegetative burning impact in the fine particle mode have been also compared by Cooper⁴ and Core.⁴⁷ On larger data sets, results from multivariate statistical techniques can be evaluated in relation to CMB results averaged over the same time period. In each case, the investigators must use their knowledge of the strength and weaknesses of the methods to determine the true source strength mix.

6.4 Analysis of Anomalous Results

The evaluation of unexpected results or contradictions between CMB results and other source strength indicators can provide extremely valuable insights into the nature of the airshed's source mix and their relative impacts. Dzubay's²⁴ investigations into unusually high concentrations of Al, K, Sr, Sb, and Ba led to identification of July 4, 1976 fireworks displays as a strong (although short-lived) particulate matter source. Cooper's²⁰ evaluation of unaccounted for fine particulate carbon in the CMB analysis of Portland aerosol eventually led to the "discovery" of vegetative burning (woodstoves, fireplaces, domestic burning, etc.) as a major source in Portland, Oregon. Core, et. al⁴⁷ identified important

inconsistencies between CMB estimated source strengths and those predicted by dispersion models in Portland, leading to major changes in the airshed's emission inventory. The key issue here is that major benefits in understanding of the airshed and its sources can be obtained through a careful evaluation of the evidence, recognizing that no single approach is inherently correct.

7.0 CHEMICAL MASS BALANCE APPLICATIONS

The receptor oriented techniques have a wide range of potential applications in apportioning source impacts related to TSP, inhalable, fine or coarse mode particulate, and visibility impairment. Applications to control strategy development and dispersion model verification have been discussed herein, but other areas such as national policy development, NAAQS assessment, enforcement of stationary source emission controls, identification of sources of toxic pollutants, and gaseous hydrocarbon source reconciliation are also possible future uses of the technology.

A few of the potential applications are listed below as examples of how CMB and other receptor methods might be used by regulatory agencies. Since receptor methods can not identify the specific origin of all particles however, the actual application of the techniques to the scenarios noted may, or may not, be successful depending on the specific problem at hand.

° Dispersion Model Validation

The comparison of source impacts derived from dispersion models to those obtained using receptor techniques represents a new approach to dispersion model validation. Specific source (or source class) impacts estimated by both techniques can be directly compared and evaluated to identify errors in emission inventory data, modeling assumptions, and meteorology that would not be apparent using traditional model validation approaches based on particulate mass. Section 6.3 of this document discusses this application further.

° Control Strategy Tracking

The effectiveness of control strategies can be tracked using CMB-derived source impact trend analysis methods. By analyzing the ambient aerosol

source mix using receptor techniques, the actual effectiveness of control strategies can be assessed and compared to that originally predicted. Ineffective strategies can be re-evaluated with minimum impact on the community while those regulations that are effective can be more easily identified.

° Evaluations of Demonstration Control Strategy

Receptor techniques can be used to identify changes in source impacts resulting from trial control strategy applications. The State of Oregon, with EPA support, is conducting studies of the effectiveness of street cleaning strategies using CMB methods to monitor changes in soil and road dust impacts.

° Growth Management

Emission inventory projections based on estimates of future community growth can be tracked over time to determine if the projections are correct compared to receptor method results based on true source impacts. By establishment and routine operation of monitoring networks designed to capture aerosol samples in a manner suitable for future receptor model analysis, the analyst has access to the historical record of trends in source impacts with which more accurate growth management decisions can be made.

° PSD Increment Tracking and Analysis

An important part of any PSD preconstruction impact analysis focuses on the assessment of a facility's projected emissions on PSD increments and NAAQS attainment plans. While dispersion models must be used for the initial impact analysis, receptor models can be used to evaluate the initial impact estimates. Comparisons of expected and actual impacts, as measured with receptor models, can form the basis upon which emission management policies can be redirected.

° Emergency Action Plan Development

Receptor source apportionment techniques are especially well suited to the identification of source impacts during air pollution episodes. It is under these acute conditions of poor dispersion and high particulate concentrations that receptor methods can more appropriately be applied than source models. Dispersion models often cannot be used because of their sensitivity to low wind speeds and difficulty in developing an adequate emission inventory. Episode monitoring data and receptor technique analysis can provide important information needed to develop and track the effectiveness of emergency action plans.

7.1 Visibility Source Apportionment

The identification of source impacts on visibility reduction has been a subject of considerable interest to regulatory agencies for many years as the public's perception of a community's air quality is often based largely on this criterion. The apportionment of source impacts on visibility reduction may be of central importance to the objectives of particulate control strategies designed to achieve NAAQS. Researchers have identified fine particulate in the light scattering range (0.1 to 1.0 μm) as the most important component associated with visibility reduction, although NO_2 provides an additional potential of discoloration caused by absorption of blue light.

As a first step, the relative importance (regression coefficient) of species in the aerosol to the total light extinction (scattering and absorption coefficients) is determined through regression analysis. Source contributions to the fine particulate mass are then identified by CMB, or other receptor methods. The CMB source impact information is then used to estimate the portion of elemental

carbon associated with auto exhaust, diesel emissions, vegetative burning and other sources. By weighting the CMB assigned species with the regression coefficient, estimates can be made as to the likely portion of the light extinction associated with specific source categories.

° Heisler¹² conducted linear regression analysis in which the particle scattering coefficient (B_{scat}) was regressed against concentrations of fine particulate species to determine if any of the components were especially important. Results from the Denver Haze Studies concluded that while no single chemical specie was uniquely efficient at scattering light (on an equivalent concentration basis), elemental carbon's ability to absorb light (B_{abs}) provided the strongest single correlation with light extinction.

° Studies by Macias⁴⁸ combined results from CMB analysis of fine particulate mass in the Southwest with concurrent light scattering (B_{scat}) measurements to determine a visibility "budget." Results indicated that sulfates accounted for nearly one-half of the scattering on a typical, clear day.

The chemical composition of the light scattering aerosols provides a valuable clue regarding their potential source.⁴⁹ Unfortunately, the ability to resolve sources of the fine particulate mass using CMB is limited when the aerosol is dominated by secondary sulfate, nitrate, ammonium ion, organic and elemental carbon species. The current inadequacy in source composition data, especially for carbonaceous components, and the absence of currently known "tracers" limit current applications to sources with more distinct fingerprints. Light extinction associated with many industrial sources may potentially be identified using these techniques however.

Future applications of this approach, based on light extinction-aerosol CMB analysis in Class I PSD areas, could add significantly to our understanding of source contributions to visibility reduction.

7.2 Chemical Mass Balance Case Studies

In the past 10 years, variations of the basic CMB approach to particulate source impact apportionment have been applied in at least 37 studies within the United States. Although most of these applications were designed to provide a general knowledge of aerosol composition and likely source contributions, results from at least five of the programs have had direct input to control strategy development in primary and secondary particulate standard nonattainment areas. Source impacts resolved during these studies include:

Crustal sources	- soil and road dust, rock crushing, coal flyash
Transportation	- leaded, unleaded auto exhaust, diesel exhaust
Vegetative burning	- residential wood combustion, land clearing, slash burning, etc. (estimate have high uncertainties)
Calcium sources	- cement dust, limestone, slag dust
Marine aerosol	
Residual oil combustion	
Iron and steel production	
Ferromanganese production	
Hog fuel boilers	
Kraft and sulfite recovery boilers	
Aluminum production	
Paint pigments	

Smelters (lead, copper and zinc)
Municipal refuse incineration
Secondary sulfate, nitrate, carbon

Although coal flyash can be resolved from crustal sources in some airsheds, the ability of the CMB model to resolve these two sources is highly dependent upon the chemical similarity of the coal flyash and local soil, as well as the proper choice of species analyzed. Quantitative estimates of source contributions for the above components can be identified with average relative uncertainties ranging from ± 5 to $\pm 30\%$, depending on the source class and its relative strength.

Brief descriptions of a few of these studies are included below as examples of the change in the technology and the frameworks within which the method has been used. Table 20 is a summary of results from many of the studies listed below. Note that not all of the sources or components listed in Table 20 were included in all studies listed.

7.2.1 Particulate Source Apportionment Studies

The following studies were research efforts which have used CMB methods to better understand source strength, develop receptor model techniques and provide basic data on the nature of the aerosol problems.

Pasadena, California

In one of the first applications of the CMB concept, S. K. Friedlander¹³ used total particulate data from Pasadena to resolve contributions from sea salt, soils, auto exhaust, fly ash, cement and tire dust using source composition data from the work of Miller¹⁴ and samples of local soils. Eighteen elements were measured by Instrumental Neutron Activation Analysis (INAA) and atomic absorption

Table 20. Urban Aerosol Sources Identified by Chemical Mass Balance
(% of Total Suspended Particulate Mass)

Source Name	Washington DC (1)	Portland OR (2)	St. Louis MO (3)	Medford OR (4)	Pasadena CA (5)	Chicago IL (6)	Denver CO (7)	Riverside CA (8)
Soil Dust	31	53.7	30	30	11.4	18	28.4	22.8
Coal Combustion	8	-	-	-	-	6.4	-	-
Refuse Incineration	1.8	-	-	-	-	-	0.4	-
Auto Exhaust	12.6	6.7	6.0	2.8	8.2	2.8	16.1	3.1
Sea Salt	1.3	2.3	-	-	1.3	-	-	1.0
Residual Oil Combustion	1.0	0.7	-	-	0.1	1.4	-	0.1
Sulfate (a)	17.7	4.1	35	1.9	-	11.5	9.1	9.2
Nitrate	3.7	4.1	-	3.0	-	5.3	-	10.3
Vegetative Burning	-	8.5	-	31.9	-	-	-	-
Metal (s) Industry	-	2.4	1.2	-	-	3.9	-	-
Hog Fuel Boilers	-	0.2	-	10.9	-	-	-	-
Paper Production	-	0.1	-	-	-	-	-	-
Tire Dust	-	-	-	-	0.8(c)	-	-	0.3(c)
Calcium Sources (b)	-	1.7	13.0	1.6	1.7	3.2	1.5	1.8
Organic Carbon	-	6.6	-	-	-	-	-	19.8
Elemental Carbon	-	1.9	-	1.1	-	-	-	-
Other	-	-	0.6	9.7	11.8(c)	-	6.0	23.0(c)
Percent Accounted For	77	93	87	93	35.3	52.5	61.5	91

(a) includes NH_4SO_4

(b) includes cement dust, limestone and other "calcium" sources

(c) emission inventory scaling to auto exhaust

(1) summer 1974 average: Reference 27

(2) annual average, downtown Portland: Reference 50

(3) July-August 1976 average of ten sites: Reference 24

(4) April-June 1979 average downtown Medford, Oregon: Reference 22

(5) September 3, 1969: Reference 14

(6) average of 22 sites on April 4, 1968: Reference 51

(7) annual average 1979 for particles $<15 \mu\text{m}$ only. Data represents sum of fine and coarse mode CMB results: Reference 12

(8) California ACHEX study; September 20, 1972: Reference 52

methods. The tire dust component was determined indirectly by assuming that the mass ratio of tire rubber to exhaust was 1:10. Altogether, about 70% of the total particulate mass was accounted for within the source classes studied.

Chicago, Illinois

In total particulate source apportionment studies by D. F. Gatz,⁵¹ 24-hour TSP samples from 20 sites were analyzed for 20 elements. Using the CMB in the "tracer" mode (see Section 3.1.1), six source classes were identified as important contributors to the aerosol mass: coal combustion, coke production, fuel oil combustion, auto exhaust, iron and steel manufacturing and cement dust. Source composition data published by Winchester and Nifong⁵³ were used in the analysis. Gatz accounted for 52% of the total particulate mass (including sulfate and nitrate ion) but carbon emissions, non-carbonate carbon components and secondary aerosols were not accounted for, nor were all potential sources included in the study. Elemental concentrations predicted by CMB were within a factor of 2 for Br, Co, Cr, Cu, Fe, and K, but As, Cd, Cl, Hg, La, Mg, Na, Se and Zn were underestimated.

Los Angeles Basin, California

The California Aerosol Characterization Study⁵⁴ (ACHEX) was conceived as one of the most comprehensive aerosol field studies yet conducted. Primary source contributions were estimated using the CMB method in its "tracer" mode supplemented with (a) emission inventory scaling techniques for those sources for which no tracer data were available, and (b) estimates of gas to particle conversion of sulfate, nitrate, organics and ammonium ion. The CMB model was used to calculate source impacts for Pasadena, Riverside, San Jose, Fresno and Pomona using Instrumental Neutron Activation Analysis (INAA) and x-ray fluorescence

(XRF) data from hi-vol and Lundgren impactor samples. Sea salt, soils, auto exhaust, cement and fly ash components were resolved by CMB. Estimates for diesels, industry and aircraft emissions were estimated by inventory ratioing techniques. Carbon balance methods were added to identify source impacts based on estimates of the percent carbon in source emissions. About 35% of the measured mass was accounted for with good CMB predicted/observed ratios for Al, Na, Ca, V, Pb, Mg and K.

St. Louis, Missouri

Size resolved particulate data from ten sites operated in St. Louis between 1975 to 1977 were used by Dzubay²⁴ to identify contributions from crustal sources (soils, road and quarry dust and fly ash), limestone, ammonium sulfate, motor vehicles, paint pigments and steel manufacturing. Ambient, dichotomous impactor samples were analyzed by XRF for elements of atomic numbers 13 to 38 plus Cd, Sn, Sb, Ba and Pb.

Source composition data consisted of data from tunnel studies by Pierson⁵⁵ and crustal, paint pigment and steel components values from the literature. Dzubay was able to account for an average of 78, 87 and 96% of fine, total particulate and coarse fractions. Elements not predicted within a factor of 2 included V, Cr, Ni, Cu, Zn, Se, Cd, Sn, Sb and Ba.

Washington, D.C.

Kowalczyk, et. al¹⁷ applied CMB methods to hi-vol total suspended particulate samples (using a 0.4 μ m Nucleopore substrate) analyzed by INAA for 27 elements. The aerosol mass was apportioned into six components: coal fly ash, oil and refuse combustion, marine aerosol, soils and motor vehicles. Eight

fitting elements (Na, V, Zn, Pb, Al, Fe, Mn, As) were used with the least squares fitting approach (see Section 3.1.2). Only stable, non-volatile elements were selected as fitting specie, serving to identify aerosol from a specific source (e.g., Pb for auto exhaust, Al for soils, etc.). Source composition data was obtained from local source tests (coal, oil and refuse combustion and soils) while marine and auto exhaust was taken from literature values.

Later work by Gordon, Zoller, Kowalczyk and Reingrover⁴⁶ improved source composition data through numerous tests of local power plants and other sources. Forty elements measured by INAA provided a CMB-predicted to observed ratios of between 0.7 and 1.5 for most elements. Underestimated elements such as K, Mg, Cr, Cu and Ni suggest that either (a) several important sources have not been identified, or (b) errors are present in the source composition data. About 48% of the TSP can be accounted for with primary aerosol emissions, the remainder consisting of secondary aerosols ($\text{SO}_4^{=}$, NO_3^- , NH_4^+) and condensible organic emissions.

Buffalo, New York

The State of New York, working in association with EPA, conducted a study of particulate source contributions in the Buffalo-Lackawana¹⁸ area between January 1978 and July 1979. Five hundred and fifty size resolved samples were analyzed by XRF for 12 elements and 10 ions. CMB was used to identify iron and steel manufacturing, soils, lime, oil and refuse combustion and auto exhaust. Fine particle mass ($\leq 4 \mu\text{m}$) was underpredicted by the CMB model by 14-23% and the coarse fraction (4-15 μm) was overestimated by 32 to 90%.

Source composition data for total particulate fraction was obtained from the Washington, D.C. studies.¹⁷ The fitting element approach of Gordon⁴⁶

was used: Si for soils, Fe for steel production, V for fuel oil combustion, Zn as a tracer for refuse incineration, Pb for auto exhaust and Ca as an indicator of concrete abrasion, cement and slag dust. CMB analysis was based on average aerosol composition data rather than 24-hour concentrations.

Denver, Colorado

Chemical mass balance was applied in the Denver airshed during the winter, 1978 studies of visibility impairment.¹² Size resolved samples taken on teflon and quartz filters were analyzed by INAA and XRF for elements and two carbon classes (organic and elemental) to resolve auto exhaust, coal combustion, residual oil combustion and soils. Diesel emissions, natural gas and unleaded auto exhaust were identified by emission inventory scaling (see Section 4.4). Secondary ammonium sulfate and nitrate were also measured. Most of the aerosol mass was apportioned by including oxygen, hydrogen and water in the estimates. Underpredicted elements included Al, Cl, K, Cr, Mn, Ni, Cu, As and Se.

Source characterization for leaded auto exhaust was developed from source tests of 1970 model year cars. Coal combustion data came from literature values while residual oil combustion data taken in Portland was adjusted to the elemental composition of the crude oil use in Colorado. Soils data from the Portland studies were used.

Dzubay and Stevens⁵⁶ also conducted a chemical mass balance analysis of Denver aerosol using dichotomous sampler data analyzed by XRF methods. Ion chromatography was used to measure sulfate and nitrate ion concentrations following elemental analysis. Total carbon analysis was conducted using collocated samplers equipped with quartz filters. Using source composition data obtained from the

literature, the study attempted to describe the Denyer aerosol in terms of six components: sulfate (and related cations), motor vehicles exhaust, shale, limestone, salt and refuse incineration. Results provided good agreement between observed and predicted values for total mass and nine elements used in the fit, but K, Cr, Ni, Ca and carbon were underpredicted. About 64% of the fine mass was found to be carbon, but it could not be successfully resolved into the sources included in the analysis.

7.2.2 Control Strategy Development Applications

The following programs represent the logical extension of earlier research efforts: application of the chemical mass balance technique to evaluating which particulate emission sources should be controlled to insure that air quality standards are attained and maintained.

Portland Aerosol Characterization Program (PACS)

The primary objectives of PACS were to (a) identify the source of at least 90% of the aerosol contributing to NAAQS violations on worst-case days and on an annual average at nonattainment monitoring sites, (b) determine the source contributions to the fine ($<2 \mu\text{m}$) particle fraction, and (c) identify sources and chemical species responsible for visibility reduction in Portland.

Cooper, Watson and Huntzicker²⁰ measured 27 elements (using INAA and XRF) and other species on over 7,000 size resolved samples, completing 1700 CMB calculations. Thirty-seven major source classes representing 95% of the emission inventory were source-sampled to obtain local fine and coarse aerosol composition data. Ambient aerosol mass was apportioned among soil dust, motor vehicle exhaust, aluminum production, hog fuel boiler, calcium sources, steel and ferromanganese production, kraft manufacturing, marine aerosol, vegetative burning,

residual oil combustion and sulfate and nitrate ion accounting for 90% of the TSP mass and 80% of the fine particulate mass. Improvements in the CMB technique included incorporation of an effective variance least squares calculation method, and an error propagation scheme.

Although the PACS program and the DEQ's approach to dispersion model validation were widely regarded as a major step in assuring community confidence in the effectiveness of the strategy, the program did not provide the level of source impact specificity anticipated:

- ° Soil and road dust, which collectively account for 39% of the characterized TSP mass, could not be chemically differentiated from one-another. Since there are few unpaved streets in Portland, most of these particles have been assumed to originate directly or indirectly (through trackout) to paved roads.

- ° Secondary particulate matter and unaccounted for carbon (31.7% of the fine mass) could not be traced to its origin by CMB. Secondary sulfate and nitrate apparently generated by urban sources, were apportioned in relation to the percent of local SO_2 (or NO_2) emitted by each source class.

- ° Approximately 21% of the fine mass and 8% of the characterized TSP mass was identified but assumed to be composed of water, NH_4^+ and analysis uncertainty.

- ° The specific sources of vegetative burning impact (20% of the fine and 15% of the TSP mass) could not be chemically determined. Emission

inventory and source activity data have, however, been used to identify the source class most likely to have been responsible.

° Specific impacts from diesel emission, distillate home heating, tire rubber, pollen, paint fragments, paper home refuse combustion and a host of other potential (and likely sources) was not chemically identified.

Figure 7 illustrates the annual average impact of aerosol sources in Portland as determined from the PACS study. The limitations in the study results reflect the current state-of-the-art in CMB analysis and serve to emphasize the importance of other, independent information in identifying specific source impacts.

Willamette Valley Studies

The objectives of the Willamette Valley study were to (a) identify the particulate impact of field burning and as many other sources as possible in relation to NAAQS, (b) provide data on fine particle source impacts to support health effect studies, and (c) determine the burning's impact on visibility reduction. The study design focused on identification of source impacts using CMB methods developed during PACS and dispersion modeling approaches to source reconciliation and strategy development.

A two year, \$611,000 coordinated program of air quality, meteorological, source characterization and dispersion model development was developed which included both ground and aircraft monitoring programs. The ground monitoring program consisted of ten sites operated on a daily basis during the summer of 1968, resulting in 2,000 size-resolved samples, which were analyzed for 18 elements, 8 ions and carbon. Chemical mass balance was conducted on about 100,

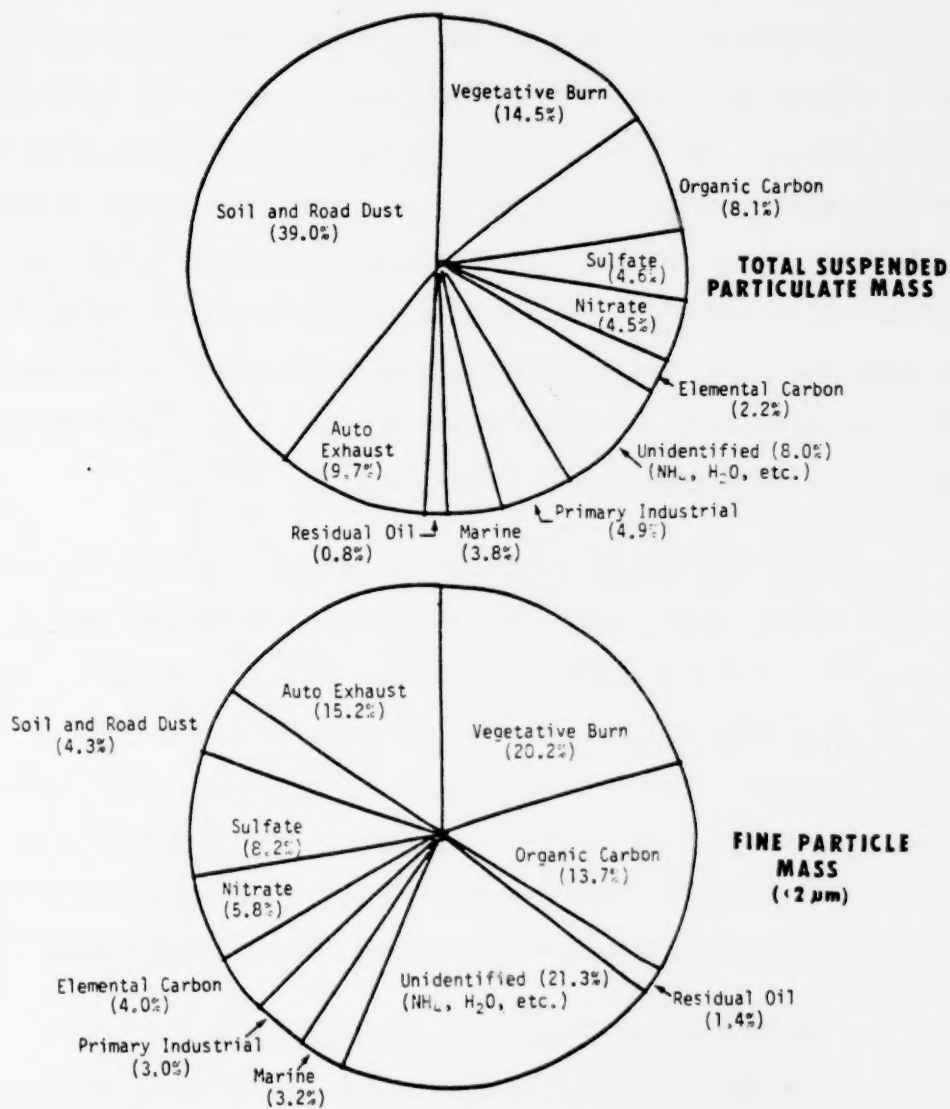


Figure 7. Aerosol Source Impacts in Downtown Portland, Annual Average

Source: Cooper, et. al (Reference 20)

24-hour samples selected on the basis of a burning activity and observed impact. Source composition data developed during PACS was supplemented with local soil data, updated vegetative burning composition information and three new industrial source classes. The aerosol mass was resolved into soil dust, motor vehicle exhaust, kraft recovery furnace emissions, vegetative burning, residual oil combustion, marine aerosol, sulfate, nitrate and residual carbon typically accounting for 90% of the fine particle mass and overestimating the coarse mass by about 20%. The impact of field burning, soil, marine air and motor vehicles was also estimated by enrichment factor analysis, "tracer mode" CMB methods and statistical techniques based on burning activity.^{57,58}

Results released to all involved parties, the State legislature and to the EPA, clearly demonstrated the importance of soil and road dust as a major source contributing to standard violations. Smoke from the burning of grass fields and timber slash was found to have short term, acute impacts. Annual impacts, however, were estimated to be less than $2 \mu\text{g}/\text{m}^3$. The findings of the study provided the first technical assessment of the impacts of grass field burning in the 20 year history of the controversy and has channeled legislative and regulatory energy into more constructive, less emotional, areas.

Medford Aerosol Characterization Study (MACS)

The Medford Air Quality Maintenance Area was designated as a primary particulate nonattainment area because of continued violations of the 24-hour and annual primary NAAQS. Located in the Bear Creek Valley of Southwest Oregon, the AQMA suffers from frequent periods of air stagnation, low wind speeds, and annual geometric mean TSP levels approaching $100 \mu\text{g}/\text{m}^3$. Control of the predominant industrial point sources has a long history which has resulted in

improved air quality. Particulate air quality standards are not, however, likely to be attained as a result of the control of traditional sources. As in Portland and the Willamette Valley, community and industry plans to expand the economic growth of the area were being restricted by the capacity of airshed to assimilate the associated increase in emissions. This prompted legislative requests to identify the relative source contributions through a comprehensive source apportionment program, develop the data base needed to support appropriate control actions and prepare SIP revisions.

Building on experience gained through the PACS and Willamette Valley programs, the Oregon Department of Environmental Quality developed a third study design costing \$215,000 over a two-year period. Again, emission inventory, meteorological and air monitoring programs were improved to insure that the CMB results for Medford could be compared to those derived from dispersion modeling. Project management, source testing, ambient sampling and some laboratory analysis functions were assumed by Department staff while trace metal (XRF, INAA) carbon analysis, CMB computations, data analysis, and reporting tasks were performed by a contractor. During the field sampling period of April 1979 to April 1980, dichotomous samplers at four sites collected aerosol samples for analysis of carbon (organic and elemental), $\text{SO}_4^{=}$, NO_3^- , Cl^- , NH_4^+ , and 25 elements.

The fine and coarse mode source composition data used in the study was derived from sampling local soils, home fireplaces and wood stoves, road dust, particle board dryers, hogged fuel boilers, charcoal manufacturing and orchard heating emissions. Motor vehicle emissions for diesels, leaded and unleaded gasoline were obtained from the literature and weighted to reflect the Medford traffic mix.

The fine and coarse particulate mass was apportioned into the eight source classes noted above, sulfate, nitrate, and residual carbon. Unlike the PACS and Willamette Valley study results, the results of the MACS program showed that many of the acute TSP episodes were related to wood burning emissions rather than soil and road dusts. Conclusions from the study have directed agency resources toward studies to minimize emissions from residential wood heating, completion of telephone surveys needed to improve wood burning emission inventories and improvements to dispersion model results.

Montana and Idaho Studies

Missoula, Montana

Studies of winter aerosol composition and source impacts using CMB,⁵⁹ optical microscopy and x-ray diffraction⁶⁰ were conducted in the Missoula non-attainment area. Sponsored by EPA Region VIII, the State of Montana and the Missoula City, County Health Department, the CMB study apportioned the fine particle fraction into residential wood combustion, soil, auto exhaust, hog fuel boiler and other sources. Results are being used in control strategy development by State and local regulatory agencies.

Kellogg, Idaho

Chemical mass balance, and other receptor models, have been applied to source resolution within the Kellogg, Idaho lead nonattainment area to identify the source impacts of lead and zinc smelters, auto exhaust and other sources. Upon completion in 1981, results from this program will provide a foundation for the airshed control strategy development. The work is being sponsored by EPA Region X and the State of Idaho.

Lewiston, Idaho

Studies of the impact of the pulp and paper manufacturing industry in the Lewiston particulate nonattainment area have been used to assess the need for further control of process emissions. Results from the industry-sponsored study have been presented to the State of Idaho Department of Health and Welfare during a contested case hearing on the need for new control systems.

Although the CMB receptor model's application to source impact identification is still undergoing development, it is clear that it will serve as a useful compliment to more classical modeling procedures. Results from studies using CMB, and other receptor models, are being used to shape regulatory programs in Oregon, Idaho, Montana and New York. Future programs to extend application of CMB to Philadelphia and Houston, as well as further analysis of Portland and Washington, DC data are planned.

7.3 Dispersion Modeling Validation

Chemical Mass Balance source strength estimates have been compared to dispersion model estimates in only a few studies. Gordon⁴⁶ has compared Washington, DC refuse incineration impact derived by CMB to box model estimates with reasonable agreement ($0.83 \mu\text{g}/\text{m}^3$ versus $0.58 \mu\text{g}/\text{m}^3$, respectively). The State of Oregon Department of Environmental Quality, Air Quality Control Division staff has devoted considerable resources to comparing, analyzing and improving dispersion model performance based on CMB results obtained during the Portland, Medford and Willamette Valley aerosol characterization studies.^{20,22,61} Core⁴⁷ and Hanrahan's⁶² review of this work has concluded that the application of CMB-derived source strength (for selected source classes) to dispersion model simulations can provide considerable insight into deficiencies in modeling assumptions,

emission inventory and source operating schedule errors. Figure 8 shows initial model predictions of paved and unpaved road dust derived from CMB analysis versus model predicted values at five sampling sites. The consistent underprediction of the model was expected, considering the difficulty in accurately inventorying fugitive dust sources. Following improvements to the inventory, utilizing a land use specific paved road dust emission factor, dispersion model predictions of road dust impact improved dramatically. Overall dispersion model annual prediction results also compared more favorably with observed TSP data (Figure 9).

In two other Oregon nonattainment areas, similar programs were undertaken to improve and validate dispersion modeling results. In both cases, major improvements in model performance were achieved through programs designed to upgrade emission inventory source categories found to be deficient through CMB-dispersion model comparisons. Road dust emission inventory improvements resulted in a 600% increase in the Portland road dust emissions inventory. A 2,000 ton per year reduction in the Eugene, Oregon's inventory occurred following collection of new traffic data on unpaved roads.

It is important to note that only CMB results for carefully selected source classes should be used for dispersion model validation.⁶³ To date, source classes used in this manner have been limited to motor vehicle exhaust, residual oil combustion, urban dust, residential wood burning, and refuse incineration, although any source whose emission composition contains two or more unique specie ratios (fingerprint) could be used.

Figure 8
Portland, Or. Dispersion Model -
Predicted Road Dust Impact*

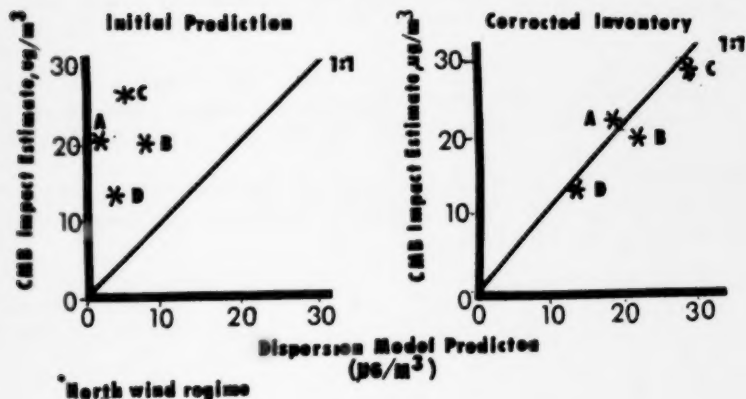
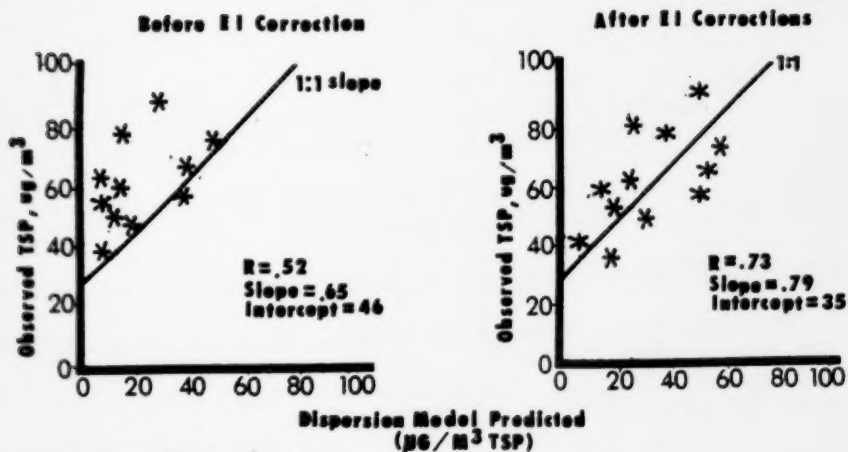


Figure 9
Portland, Or. Dispersion Model
Annual Average Prediction



Source: Cora, et al. (Ref. 47)

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APPENDIX I

Abbreviations of Chemical Elements and Species

Abbreviation	Chemical Element	Abbreviation	Chemical Element
Al	aluminum	Mg	magnesium
Sb	antimony	Mn	manganese
As	arsenic	Hg	mercury
Ba	barium	Mo	molybdenum
Be	beryllium	Ni	nickel
Bi	bismuth	N	nitrogen
B	boron	NO ₃ ⁻	nitrate ion
Br	bromine	O	oxygen
Cd	cadmium	P	phosphorus
Ca	calcium	K	potassium
C	carbon	Rb	rubidium
OC	organic carbon	Sc	scandium
EC	elemental carbon	Se	selenium
Cs	cesium	Si	silicon
Cl	chlorine	Na	sodium
Cr	chromium	Sr	strontium
Co	cobalt	S	sulfur
Cu	copper	SO ₄ ⁻²	sulfate ion
F	fluorine	Th	thorium
H	hydrogen	Sn	tin
I	iodine	Ti	titanium
Fe	iron	W	tungsten
La	lanthanum	V	vanadium
Pb	lead	Zn	zinc
Mg	magnesium		